
Research and Development



Handbook for Sampling and Sample Preservation of Water and Wastewater



HANDBOOK FOR
SAMPLING AND SAMPLE PRESERVATION
OF WATER AND WASTEWATER

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

This report has been reviewed by the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement.

FOREWORD

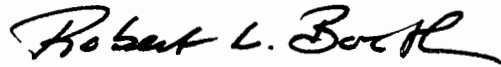
Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati:

- o Develops and evaluates techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- o Investigates methods for the concentration, recovery and identification of viruses, bacteria, and other microbiological organisms in water. Conducts studies to determine the responses of aquatic organisms in water.
- o Conducts an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

Standardized analytical methods and quality control procedures become academic if samples are not representative of their original environment or if constituents change between time of sampling and analysis. This publication provides guidelines and recommendations on techniques for sampling and sample preservation to help alleviate these problems. Procedures have been standardized as much as possible throughout this document. However, sampling techniques cannot be predetermined for all situations, so the use of statistical procedures to establish location and frequency of sampling, number of samples, and parameters to be analyzed is recommended when other guidelines do not exist. Sample preservation methods and holding times are included for the parameters listed for the National Pollutant Discharge Elimination System and Primary Drinking Water Regulations. Special handling or sampling techniques are also included for the individual constituents. Personnel establishing a sampling program should find sufficient information to determine the best techniques to apply.

This manual can not detail all aspects of sampling for water and wastewater samples, therefore, references are provided for further study in areas of interest.

Finally, the guidelines and recommendations are not intended to supercede EPA enforcement requirements, rather to provide information to sampling personnel. Sampling and sample preservation requirements for inhouse and extramural projects, compliance monitoring and enforcement proceedings, and other mandatory activities are specified by the responsible program.

A handwritten signature in black ink, reading "Robert L. Booth". The signature is written in a cursive style with a large, stylized "R" and "B".

Robert L. Booth
Acting Director
Environmental Monitoring & Support
Laboratory - Cincinnati

ABSTRACT

The four basic factors which affect the quality of environmental data are sample collection, sample preservation, analyses, and recording. Improper actions in any one area may result in poor data from which poor judgements are certain. This manual was developed to provide general and specific guidance in sample collection and preservation.

A review of the literature and a survey of field practices provide the basis for guidelines in general sampling techniques, samplers, flow measuring devices, a statistical approach to sampling, preservation of samples for physical, chemical, biological and radiological analyses, procedures for sampling waters from municipal, industrial, and agricultural sources, surface waters, and sludges.

Finally this handbook does not supersede sampling, preservation, or chain of custody procedures specified by enforcement, compliance monitoring, or program offices of the U.S. Environmental Protection Agency. Rather it is intended to complement their requirements.

CONTENTS

Foreword	iii
Abstract	v
Acknowledgement	xi
1. Introduction	1
2. General Considerations for a Sampling Program	2
2.1 Objectives of Sampling Programs	2
2.2 Sampling Locations	4
2.3 Sample Collection Methods	6
2.4 Type of Sample	19
2.5 Planning a Sampling Program	30
2.6 Field Procedures	37
2.7 References	39
3. Flow Measurements	41
3.1 Closed Conduit Flow Measurement	41
3.2 Flow from Pipes Discharging to the Atmosphere	53
3.3 Open Channel Flow Measurements	57
3.4 Miscellaneous Flow Measurement Methods	81
3.5 Secondary Devices	88
3.6 References	102
4. Statistical Approach to Sampling	105
4.1 Basic Statistics and Statistical Relationships	105
4.2 Determination of Number of Samples	141
4.3 Determining Sampling Frequency	144
4.4 Determination of Parameters to Monitor	146
4.5 In-Plant Sampling and Network Monitoring	154
4.6 References	168
5. Sampling Municipal Wastewaters	170
5.1 Background	170
5.2 Objectives	170
5.3 Frequency of Sampling	170
5.4 Location of Sampling Points	171
5.5 Number of Samples	176
5.6 Parameters to Measure	177
5.7 Type of Sample	177

5.8	Methods of Sampling	177
5.9	Volume of Sample and Container Type	178
5.10	Preservation and Handling the Samples	178
5.11	Flow Measurements	179
5.12	References	179
6.	Sampling Industrial Wastewaters	180
6.1	Background	180
6.2	Objectives of Sampling Programs	180
6.3	Frequency of Sampling	181
6.4	Location of Sampling Points	181
6.5	Number of Samples	183
6.6	Parameters to Measure	183
6.7	Type of Sample	186
6.8	Method of Sampling	186
6.9	Volume of Sample and Container Type	187
6.10	Preservation and Handling of Samples	187
6.11	Flow Measurement	187
6.12	References	187
7.	Sampling Agricultural Discharges	188
7.1	Background	188
7.2	Objectives	188
7.3	Frequency of Sampling	188
7.4	Location of Sampling Points	189
7.5	Number of Samples	189
7.6	Parameters to Analyze	189
7.7	Type of Sample	190
7.8	Method of Sampling	190
7.9	Volume of Sample and Container Type	190
7.10	Flow Measurement	190
7.11	References	194
8.	Sampling Surface Waters, Aquatic Organisms and Bottom Sediments	195
8.1	Background	195
8.2	Objectives of the Study	195
8.3	Parameters to Measure	195
8.4	Location of Sampling Points	195
8.5	Random Sampling	200
8.6	Frequency of Sampling	203
8.7	Method of Sampling	203

8.8	Types of Samples for Aquatic Organisms	203
8.9	Volume of Sample and Container Type	203
8.10	Preservation and Handling of Samples	217
8.11	Flow Measurement	217
8.12	References	217
9.	Sampling of Ground and Drinking Water	218
9.1	Background	218
9.2	Objectives of Ground Water Sampling	218
9.3	Ground Water Subsurface Characteristics	219
9.4	Location of Ground Water Sampling Points	220
9.5	Construction of Ground Water Monitoring Wells	227
9.6	Collection of Ground Water Samples	234
9.7	Sampling Ground Water Subsurface Solids	250
9.8	Preservation and Handling Procedures for Ground Water Parameters	251
9.9	Sampling of Drinking Water	255
9.10	References	267
10.	Sampling Sludges	269
10.1	Background	269
10.2	Objectives of Sampling Programs	269
10.3	Parameters to Analyze	270
10.4	Location of Sampling Points	270
10.5	Frequency of Sampling	272
10.6	Number of Samples	272
10.7	Type of Sample	272
10.8	Method of Sampling	273
10.9	Volume of Sample and Container Type	273
10.10	Preservation and Handling of Samples	273
10.11	Flow Measurement	273
10.12	References	273
11.	Suspended Solids Sampling	275
11.1	Representative Sampling Theory	275
11.2	Segregation Sampling Error	275
11.3	Field Sampling	280
11.4	Laboratory Subsampling	281
11.5	Guidelines of Sampling of Suspended Solids	285
11.6	References	285

12. Sampling, Preservation and Storage Considerations for Trace Organic Materials	286
12.1 Sample Collection Method	292
12.2 Sediment Sampling	293
12.3 Sampling Location	303
12.4 Sample Container	303
12.5 Sampling Procedure and Pretreatment of Sample Equipment	305
12.6 Sample Preservation and Storage	306
12.7 References	310
13. Sampling Radioactive Materials	313
13.1 Background	313
13.2 General Considerations	315
13.3 Frequency of Sampling	316
13.4 Location of Sampling	318
13.5 Sample Volume	318
13.6 Sample Containers	319
13.7 Sample Filtration	319
13.8 Sample Preservation	320
13.9 General Sampling Procedure - Water & Wastewater	320
13.10 Radiation Safety	321
13.11 References	321
14. Collecting and Handling Microbiological Samples	323
14.1 Background	323
14.2 Analytical Methodology	323
14.3 Sample Bottle Preparation	326
14.4 Sample Methods and Equipment	327
14.5 Sample Frequency and Site Selection	337
14.6 Preservation and Transit of Samples	343
14.7 References	344
15. Sample Control Procedures and Chain of Custody	345
15.1 Sample Identification	345
15.2 Chain of Custody Procedures	348
15.3 Field Notes	355
15.4 References	355

16. Quality Assurance	356
16.1 Objectives of Quality Assurance Program	356
16.2 Elements of a Quality Assurance Plan	357
16.3 Personnel Training	357
16.4 Quality Assurance in Sampling	359
16.5 EPA Quality Assurance Program	365
16.6 References	367
17. Sample Preservation	368
17.1 Methods of Preservation	368
17.2 Containers	394
17.3 Holding Time	397
17.4 Sample Volume	397
17.5 References	397
Appendix A	401
Appendix B	402

ACKNOWLEDGEMENT

The material in this handbook covers a wide range of subject areas with respect to Sampling and Sample Preservation of waters and wastewaters. Many people, too numerous to list, made worthwhile contributions to the successful completion of this Handbook. However, I wish to express my appreciation and special thanks to the following:

- (a) Envirex, Inc., who provided the original contract report, EPA 600/4-76-049, upon which this handbook was built.
- (b) Bionetics, Inc., particularly, V. Kowalski, A.J. DiPuccio, T.V. Gala and other administrative and clerical personnel, who were responsible for conducting an extensive literature search and condensing the information into subsequent chapters in this handbook.
- (c) U.S. Environmental Protection Agency Personnel, M.R. Scalf, J.F. Cosby; and Robert S. Kerr Environmental Research Lab, Ada Oklahoma, for authoring the chapter on ground water sampling.
- (d) U.S. Environmental Protection Agency personnel, J.W. Winter, R.H. Bordner, EMSL-Cincinnati, for authoring the chapter on microbiological sampling.
- (e) U.S. Environmental Protection Agency personnel, R.L. Graves and H.E. Kolde, for authoring the chapters on trace organics and radiological sampling, respectively.
- (f) U.S. Environmental Protection Agency, P. Britton for his valuable input and editing of the statistics chapter.
- (g) U.S. Environmental Protection Agency, E.L. Berg, EMSL-Cincinnati for authoring chapters on drinking water, flow measurement, and suspended solids.
- (h) Finally, special thanks to the over 250 reviewers representing the federal, state and local governments, commercial manufacturers of sampling equipment, industry, and engineering consulting firms.

Editor

Edward L. Berg

Edward L. Berg, P.E.

Environmental Monitoring & Support Laboratory

U.S. Environmental Protection Agency

Cincinnati, Ohio

CHAPTER 1

INTRODUCTION

Obtaining representative samples and maintaining their integrity are critical parts of any monitoring or enforcement program. Analytical methods have been standardized but the results of analyses are only as good as the sampling and the sample preservation methods. The purpose of this handbook is to present the best techniques currently available for sampling and sample preservation. The recommendations were developed after an extensive literature review and survey of current laboratory and field practices. The handbook will allow personnel to determine the most effective procedures for their specific applications.

In sampling, the objective is to remove a small portion of an environment that is representative of the entire body. Once the sample is taken, the constituents of the sample must stay in the same condition as when collected. The length of time that these constituents will remain stable is related to their character and the preservation method used.

The sampling technique is determined by the type of water or wastewater to be sampled. This handbook primarily addresses the water and wastewater types shown below and addresses in a limited way, sampling of oceans and estuaries..

- | | |
|------------------------------------|-------------------------|
| 1. Municipal wastewaters | 4. Agricultural run-off |
| 2. Industrial wastewaters | 5. Wastewater sludges |
| 3. Surface waters and
sediments | 6. Ground water |
| | 7. Drinking water |

General information on automatic samplers, flow monitoring and statistical methods used to determine number of samples, frequency of sampling, location of sampling, and parameters to be measured are included.

Special consideration is given to sampling for suspended solids, trace organics and radioactive substances.

Since preservation methods relate to the parameters to be analyzed, these techniques are classified by parameter.

CHAPTER 2

GENERAL CONSIDERATIONS FOR A SAMPLING PROGRAM

Most definitions of water quality are use-related. Each user produces wastewaters containing pollutants which impacts the environment in different ways. For example, power plants discharge thermal pollution that impacts the biological population, household nutrient discharges lead to eutrophication of lakes, industrial discharges cause oxygen depletion or discharge toxic substances which kill fish. The broad spectrum of ground water, surface waters, lakes, estuaries, coastal waters, municipal wastes, industrial wastewaters and surface run-offs make monitoring of water quality a formidable task. Sampling is the first key element in a monitoring program that must be performed properly to assure valid data. No single sampling program can apply to all types of waters, nevertheless, each sampling program must consider:

- | | |
|-----------------------------------|------------------------------|
| 1. Objectives of Sampling Program | 4. Sample Collection Methods |
| 2. Location of Sampling Points | 5. Flow Measurements |
| 3. Types of Samples | 6. Field Procedures |

2.1 OBJECTIVES OF SAMPLING PROGRAMS

There are four major reasons for sampling and analyses program; planning, research or design, process control, and regulation. These objectives in an overall water quality program are interrelated and cover different stages from planning to enforcement. Based upon these objectives, the different sampling programs are compared in general terms in Table 2.1. Since the objectives of a program directly affect sampling and laboratory analyses, specifying the objectives is the first step in planning a sampling program.

2.1.1 Planning Objectives

An area-wide or basin planner monitors to:

1. Establish representative baseline water quality conditions;
2. Determine assimilative capacities of streams;
3. Follow effects of a particular project or activity;
4. Identify pollutant source;
5. Assess long term trends;
6. Allocate waste load; or
7. Project future water characteristics.

2.1.2 Research Objectives

Water/wastewater research projects conduct sampling and analyses to:

1. Determine the treatment efficiency for a unit process or overall treatment system,
2. Determine the effect of changes in process control variables,
3. Characterize influent and effluent streams and sludges,
4. Optimize chemical dosages, loadings for carbon adsorption columns, for advance waste treatment processes or treatment of drinking water, or
5. Ascertain health effects of effluents, sludges, drinking waters and ambient waters.

2.1.3 Process Control Objectives

Water/wastewater treatment process and associated systems conduct sampling and analyses to:

1. Produce an effluent of the highest quality,
2. Optimize and maintain physical, chemical, and biological process control variables that affect treatment efficiency, i.e. mixed liquor suspended solids, sludge withdrawal rate, dissolved oxygen, chemical dosages, etc,
3. Determine resource recovery from unit processes,
4. Allocate the cost of treatment to a unit within a complex of unit processes, or
5. Determine substances that are toxic or interfere with the treatment system.

TABLE 2.1 COMPARISON OF SAMPLING PROGRAMS BASED ON OBJECTIVES

Objectives	Planning	Research Design	Process Control	Regulatory
Scope	General	Specific	Specific	Specific
Goals	Establish trends Benchmarks Background levels	New Developments Modifications Improvements	Operation quality control	Verification compliance enforcement
Effort	Non-intensive and unlimited	Intensive and limited	Non-intensive and limited	Non-intensive and limited

2.1.4 Regulation Objectives

Most sampling surveys and subsequent analyses are performed to meet the requirements of federal, state, or local regulations. An example of regulatory monitoring is the National Pollutant Discharge Elimination System (NPDES) established in accordance with the Federal Water Pollution Control

Act Amendments of 1977 and 1978 (P.L. 92-500). Specific objectives in collecting regulatory data vary considerably and often overlap, but generally are performed to:

1. Verify self-monitoring data,
2. Verify compliance with NPDES permit,
3. Support enforcement action,
4. Support permit reissuance and/or revision, or
5. Support other program elements such as water quality standards requiring wastewater data.

2.2 SAMPLING LOCATIONS

2.2.1 General Considerations

Usually, the sampling program objectives define the approximate locations for sampling, for example, influent and effluent to a treatment plant or water supply intake. Often, however, the sampling program objectives give only a general indication, such as the effect of a surface runoff on a river quality when assessing the quality of drinking water supplies for a community.

Since water quality varies from place to place in most water systems, locations appropriate to the information needs of a particular program must be selected. The nature and extent of spatial heterogeneity can vary with time, and can also differ markedly between systems of the same type. A typical case may be a zone where fresh and saline waters are mixing. No specific guidelines can be given on the exact locations for sampling; however, some general points are given in Section 2.2.2 and 2.2.3 when considering sampling locations.

2.2.2 Relevant Factors in Selecting Sampling Locations

The selected sampling locations must be representative sites. The term "representative point" is defined in 40 CFR, Part 35, subpart B, Appendix A, p. 224, 1976 as a location in surface waters or ground waters at which specific conditions or parameters may be measured in such a manner as to characterize or approximate the quality or condition of the water body; or a location in process waters or wastewaters where specific conditions or parameters are measured that adequately reflect the actual conditions of those waters or wastewaters.

Factors influencing the selection of sampling locations are:

- . homogeneity of the water or wastewater. Turbulence and good mixing resulting from a hydraulic jump and spring and fall turnovers of a lake, respectively, enhance the homogeneity or the uniform distribution of the constituents in the body of water.
- . Non-homogeneity of the water or wastewater. Poor mixing, for example, stratification in lakes or a river downstream of a

waste discharge. Different densities of the constituents, such as floating oils or settling suspended solids. Chemical or biological reactions, such as growth of algae in upper layers of the body of water, causing changes in pH.

- . Other considerations such as pronounced degradation of water quality in specific areas, suitability for flow measurements, convenience and accessibility.

2.2.3 Selection of Sampling Locations (1)

The selection of the location of sampling must consider:

1. Homogeneity of water or wastewater:

- . At significant outlets and inputs of lakes, impoundments, estuaries or coastal areas that exhibit eutrophic characteristics.
- . At locations upstream and downstream of major population and/or industrial centers which have significant discharges into a flowing stream.
- . Upstream and downstream of representative land use areas and morphologic zones.
- . From several locations to obtain the required information.

2. General characteristics of water or wastewater: (1)

- . At representative sites in mainstream of rivers, estuaries, coastal areas, lakes or impoundments.
- . In major water use areas, such as public water supply intakes, commercial fishing areas and recreational areas.
- . At representative sites in the individual waste streams.
- . At the mouths of major or significant tributaries to mainstreams, estuaries or coastal areas.

3. Pronounced water quality degradation:

- . At critical locations (which have the potential for displaying the most pronounced water quality or biological problems) in water quality limiting areas.
- . At critical locations within eutrophic or potentially eutrophic lakes, impoundments, estuaries, or coastal areas.

4. Flow Measurement:

- . Locations where corresponding discharges are known or can be estimated.

5. Convenience, accessibility and practicability are certainly important but they must be secondary to representativeness of sampling.

2.3 SAMPLE COLLECTION METHODS

Samples can be collected manually or with automatic samplers. Whichever technique is adopted, the success of the sampling program is directly related to the care exercised in the sample collection. Optimum performance will be obtained by using trained personnel.

2.3.1 Manual Sampling

There is minimal initial cost involved in manual sampling. The human element is the key to the success or failure of manual sampling programs. It is well suited to a small number of samples, but is costly and time consuming for routine and large sampling programs. Table 2.2 lists some of the advantages and disadvantages of manual and automatic sampling. Various types of manual grab samplers are described throughout the Handbook.

2.3.2 Automatic Samplers

Automatic samplers are being used increasingly because of their cost effectiveness, versatility and reliability, improved capabilities - greater sampling frequency, and increased sampling needs because of the NPDES permit program.

Automatic samplers are available with widely varying levels of sophistication, performance, mechanical reliability and cost. Table 2.3 lists different automatic samplers and their characteristic features.(3) However, no single automatic sampling device is ideally suited for all situations. For each application the following variables should be considered in selecting an automatic sampler: (4)

- . Variation of water or wastewater characteristics with time.
- . Variation of flow rate with time.
- . Specific gravity of liquid and concentrations of suspended solids.
- . Presence of floating materials.

Selection of a unit or a variety of units for sampling should be preceded by a careful evaluation of such factors as:

- . The range of intended use.
- . The skill level required for installation of the automatic sampler.
- . The level of accuracy desired.

References 5,6,7,8, and 9 have useful information on the theoretical design considerations and actual field performance data for automatic samplers.

TABLE 2.2 THE ADVANTAGES AND DISADVANTAGES OF MANUAL AND AUTOMATIC SAMPLING

Type	Advantages	Disadvantages
Manual	Low capital cost	Probability of increased variability due to sample handling
	Compensate for various situations	Inconsistency in collection
	Note unusual conditions	High cost of labor*
	No maintenance	Repetitious and monotonous task for personnel
	Can collect extra samples in short time when necessary	
Automatic	Consistant samples	Considerable maintenance for batteries & cleaning; susceptible to plugging by solids
	Probability of decreased variability caused by sample handling	Restricted in size to the general specifications
	Minimal labor requirement for sampling	Inflexibility
	Has capability to collect multiple bottle samples for visual estimate of variability & analysis of individual bottles	Sample contamination potential
		Subject to damage by vandals

* High cost of labor assumes that several samples are taken daily, large distances between sampling sites, and labor is used solely for sampling.

2.3.2.1 Criteria for Evaluating Automatic Sampler Subsystems

There are usually five interrelated subsystems in the design of an automatic sampler. The criteria for selecting subsystems are briefly described below; more detailed information can be found in references 5,6, and 9.

2.3.2.1.1 Sample Intake Subsystem

The success of an automatic sampler in gathering a representative sample depends on sampling site conditions (4) and the design of the sample intake subsystem. The reliability of a sample intake subsystem is measured in terms of:

- . Freedom from plugging or clogging.
- . Non-vulnerability to physical damage.

TABLE 2.3 AUTOMATIC SAMPLERS AND THEIR CHARACTERISTIC FEATURES (3)

MANUFACTURER	MODEL NO.	APPROX. COST (\$)	DIMENSIONS WD. x DEPTH. x HT. or DIA. x HT. (cms)	WEIGHT (kg)	SAMPLE BOTTLES		TYPE COOLING	MATERIALS EXPOSED TO SAMPLES			Velocity Sample Line (cm/sec)	MAX. LIFT (cm H ₂ O)	INTAKE LD. (mm)	TYPE OF PUMP	PURGE CYCLE	CONTROLS					POWER		
					No.	Cap. (ml)		Bottles	Tubing	Other						Flow Prop.	Time Prop.	Solid State	AC	Butt.	Pres.	Spring	PORTABLE or FIXED
BIF Sanitrol	41-4	670	27.3 x 25.4 x VAR.	18.16	1	7570		Nalgene	Tygon	Fiberglass		762		Dipper			X		X				F
Brailsford	EVS-3B	672	30.5 x 22.9 x 48.3	8.72	1	3785		Polypropylene	Tygon	Plexiglas	10.2	182	3.16	Vacuum			X		X	X			P
Brailsford	DC-F	296	30.5 x 24 x 48.3	8.72	1	7570		Polypropylene	Tygon	Teflon	23.2	213	3.16	Piston			X			X			P
Brailsford	DU-2	373	30.5 x 22.9 x 48.3	8.72	1	7570		Polypropylene	Tygon	Teflon	23.2	213	3.16	Piston			X			X			P
Brailsford	EP	373	Small	L	1	3785		Polypropylene	Tygon	Teflon	23.2	213	3.16	Piston			X			X			P
BVS	PP-100	700	31.8 x 25.4 x 46	35	1	9463		Plastic	Tygon	PVC		6096	3.16	Pressure			X				X		P
BVS	PPR-100	900	43.2 x 49.5 x 45.1		1	5678	Ref.	Plastic	Tygon	PVC		6096		Pressure			X			X	X		P
BVS	SE-400	2700	61 x 61 x 122	79.5	1	18,925	Ref.	Polyethylene	Plastic	PVC		975	12.7	Submersible			X	X	X				F
BVS	SE-600	2900	61 x 61 x 122	79.5	1	18,925	Ref.	Polyethylene	Plastic	PVC			50.8	Submersible			X	X	X				F
Bristol	M-4KT	941	7.6 x 30.4	3.2	1	3785		Polypropylene		Stainless				Plunger into Pipeline			X	X	X				F
Chandler	SR-10	2245	27.2 x 59.7 x 108	45.4	1	8000	Ref.	Polyethylene	PVC	U	H	671		Vacuum	X		X	X	X				F
Collins	40-2R	1343	50.8 x 61 x 122	100	1	18,925	Ref.	Polyethylene	Polyethylene	Polypropylene	H	610	9.5	Moyno			X		X				F
EMA	200 AC	239	20 x 83	9.1	1	U	Ice	U	Plastic	Aluminum		77	9.5	Solenoid Plunger			X		X	X			F
ETS	FS-4	1100	108 x 46 x 55	31.8	12	3785		Plastic		Noryl	L	883		Peristaltic			X		X				P
Fluid Kinetics	Custom Design						Ref.									X	X	X	X				F
FMC Corp.	Tru-Test	2850	49.6 x 60.4 x 131	147.6	1	7500	Ref.	Polyethylene			93.3	457	50.8	Centrifugal			X	X	X				F
Horizon	7578	600	40.6 x 23.5 x 57.2	12.7	1	9463		Polyethylene	Tygon	Silicone		914	4.8	Peristaltic			X			X			P
Hydragard	FP	370	10.2 x 74	3.2	1	U		U	Plastic	Stainless			9.5	Pressure		X	X				X		P
Hydra-Numatic	HNS	1980	91.4 x 33.4 x 91.4	90.8	1	18,925		Polyethylene	Tygon	Bronze	75	457	12.7	Impeller		X	X		X				F
ISCO	1392	1200	49.5 x 53.3	18.2	28	500	Ice	Polyethylene	Tygon	Silicone	96.3	790	6.35	Peristaltic	X	X	X		X	X			P
ISCO	1480	800	48.5 x 64.8	14.1	1	11,350	Ice	Polyethylene	Tygon	Silicone	24.1	790	6.35	Peristaltic	X	X	X		X	X			P
ISCO	1580	900	48.5 x 64.8	14.1	1	11,350	Ice	Polyethylene	Tygon	Silicone	96.3	790	6.35	Peristaltic	X	X	X	X	X	X			P
Lakeside	T2	1855		25	1	U	Ref.	U	Plastic	Plexiglas			12.7	Scoop		X			X				F
Manning	S-3000	1100	55.6 x 73.5	13.2	1	15,000	Ice	Polyethylene or Glass	PVC or Teflon	PVC or Teflon	H	670	9.5	Vacuum	X	X	X	X	X	X			P
Manning	S-4040	1700	48.3 x 57.2	17.2	24	500 1000	Ice	Polyethylene or Glass	PVC or Teflon	PVC or Teflon	H	670	9.5	Vacuum	X	X	X	X	X	X			P
Manning	S-4050	2000	48.3 x 57.2	17.2	24	500 1000	Ice	Polyethylene or Glass	PVC or Teflon	PVC or Teflon	H	670	9.5	Vacuum	X	X	X	X	X	X			P
Manning	S-5000	2800	61 x 61 x 143	73	1	19,000	Ref.	Polyethylene or Glass	PVC	PVC	H	670	16	Vacuum	X	X	X	X	X				F
Manning	S-6000	3200	61 x 61 x 143	80	24	1000	Ref.	Polyethylene or Glass	PVC	PVC	H	670	16	Vacuum	X	X	X	X	X				F
Markland	1301	1150	43.2 x 30.5 x 71.1	27.2	1	7570		Polyethylene	Tygon	E.P.T.		914	6.35	Pressure			X	X		X	X		P
Markland	2104T-CLK	1250			1	7570		U	Tygon	E.P.T.		914	6.35	Pressure			X	X	X	X			F

X - HAS, U - USER SUPPLIED, L - LOW, H - HIGH

Costs are 1975 prices, except Manning which are 1981 prices.

(continued)

TABLE 2.3 AUTOMATIC SAMPLERS AND THEIR CHARACTERISTIC FEATURES (3)

MANUFACTURER	MODEL NO.	APPROX. COST (\$)	DIMENSIONS WD. x DEPTH. x HT. or DIA. x HT. (cms)	WEIGHT (kg)	SAMPLE BOTTLES		TYPE COOLING	MATERIALS EXPOSED TO SAMPLES			Velocity Sample Line (cm/sec)	MAX. LIFT (cm H ₂ O)	INTAKE I.D. (mm)	TYPE OF PUMP	PURGE CYCLE	CONTROLS				POWER			PORTABLE or FIXED
					No.	Cap. (ml)		Bottles	Tubing	Other						Flow Prop.	Time Prop.	Solid State	AC	Batt.	P.Bat.	Spring	
N-Con	Surveyor	275	Small	L	1	U		U	U	Buna-N	H	182	12.7	Impeller			X		X				P
N-Con	Scout	520	35.6 x 15.3 x 43.2	10	1	3785		Polypropylene	Tygon	Silicone	12.1	457	6.35	Peristaltic			X		X	X			P
N-Con	Sentry	1100	40.6 x 35.6 x 33	15.9	24	450		Glass	Tygon	Silicone	12.1	457	6.35	Peristaltic	X		X		X	X			P
N-Con	Trebler	1600			1	U	Ref.	U		PVC		L		Scoop		X			X				F
N-Con	Sentinel		58.5 x 25.4 x 147.4	84	1	7570	Ref.	Polyethylene		PVC			50.8	U			X		X				F
NP Enterprises	NPE				1		Ref.				H			Vacuum	X		X		X				F
Phips & Bird	8392-300	850			1	U		U		Stainless		305		Dipper			X		X	X			F
Pro-Tech	CG-125	800	33 x 25.4 x 43.2	9.1	1	5678		TFE Resins	TFE Resins	PVC		914	3.16	Pressure	X		X				X		P
Pro-Tech	CG-150	900	33 x 25.4 x 43.2	9.1	1	5678		TFE Resins	TFE Resins	PVC		914	3.16	Pressure	X		X				X	X	P
Pro-Tech	CEL-300	1500	33 x 48.3 x 43.2	13.7	1	5678		TFE Resins	PVC	PVC	99.7	914	12.7	Submersible			X		X				P
Pro-Tech	DEL-240S	5700	76.2 x 81.2 x 182.9		24	100	Ref.	TFE Resins	Stainless	PVC	99.7	914	12.7	Submersible			X		X				F
QCEC	CVE	570	38.1 x 38.1 x 60.9	24.9	1	1893	Ice	Glass	Tygon	Plexiglas	H	610	6.35	Vacuum	X		X		X				P
QCEC	E	1000	20.3 x 33 x VAR.	45.4	1	U				Stainless				Dipper			X		X				F
QCEC	CVE II	950	38.1 x 43.2 x 38.1	15.9	1	3785	Ice	Glass	Plexiglas	Brass	H	610	12.7	Vacuum	X		X	X	X	X			P
QCEC	LF	960	39.4 x 7.7	10	1	U		U	U	Stainless				Plunger into Pipeline			X		X				F
Sigmamotor	WD-1	650	34.3 x 25.4 x 36.9	14	1	9462		Plastic	Tygon		9.7	670	3.16	Nutating			X		X	X			P
Sigmamotor	WD-5	1100	50 x 37 x 64	27	1	18,925		Plastic	Tygon		4.2	548	6.35	Finger			X		X	X			P
Sigmamotor	WM-4-24	1100	50 x 37 x 64	25.4	24	450		Plastic	Tygon		9.7	670	3.16	Nutating	X		X		X	X			P
Sigmamotor	WM-6-24	1400	50 x 37 x 64	29	24	450		Plastic	Tygon		4.2	548	6.35	Finger	X		X		X	X			P
Sigmamotor	WAP-2	700	34.3 x 25.4 x 36.9	11.4	1	9462		Plastic	Tygon		9.7	670	3.16	Nutating		X			X				P
Sigmamotor	WAP-5	1050	50 x 37 x 64	19.1	1	18,925		Plastic	Tygon		4.2	548	6.35	Finger		X			X				P
Sigmamotor	WM-1-24R	1525	53.4 x 55.9 x 86.4	56.8	24	450	Ref.	Plastic	Tygon		9.7	670	3.16	Nutating	X		X		X				F
Sigmamotor	WAC-5R	1300	53.4 x 55.9 x 125	44.5	1	18,925	Ref.	Plastic	Tygon		Var.	670	3.16	Finger		X			X				F
SIRCO	B/ST-VS	1670- 2950		127	24	473	Ref.	Polyethylene	Plexiglas		H		9.53	Vacuum	X		X		X				F
SIRCO	B/IE-VS	1100- 2778		123	1		Ref.	Stainless	PVC	PVC		6096		Dipper			X		X				F
SIRCO	B/OP-VS	1375- 2772		91	24		Ref.	Polyethylene	PVC	Plexiglas				Pressurized Source			X		X				F
SIRCO	MK-VS	675- 1364	40.7 x 40.7 x 55.9	17	1 24	15,140 500		Plastic	PVC	Plexiglas	140	670	9.53	Vacuum	X		X	X	X	X			P
Sonford	NW-3	1000	39.4 x 39.4 x 68	23.2	24	473		Glass	Tygon	Stainless		396	6.35	Evacuated Bottles			X					X	P
Sonford	HG-4	500	33.8 x 31.4 x 33.5		1	3785		Polyethylene		Stainless		53		Telescoping Tube			X		X	X			P
TMI	MARK 3B	845	36.8 x 6.6	14.5	12	570		Glass	Tygon	Stainless		300	6.35	Evacuated Bottles			X					X	P
TMI	MARK 4B	950	38 x 38 x 47	20.2	24	570		Glass	Tygon	Stainless		300	6.35	Evacuated Bottles			X			X		X	P
Tri-Aid Sciences	Custom Design						Ref.		Silicone			762	9.53	Peristaltic		X	X	X	X				F
Waste Watcher	CS/TP	1425	20 x 20 x 7	10.5	1	U		U	Tygon	Silicone	34	670	7.9	Peristaltic	X	X	X		X				F

X - HAS, U - USER SUPPLIED, L - LOW, H - HIGH

Costs are 1975 prices, except Manning which are 1981 prices.

- . Minimum obstruction to flow.
- . Capability to draw a representative sample.
- . Multiple intakes.
- . Rigid intake tubing or facility to secure or anchor the intake tubing. Avoidance of sharp bends, twists, or kinks to prevent clogging of intake line.
- . Compatible materials

2.3.2.1.2 Sample Gathering Subsystem

Three basic sample gathering methods available in commercial samplers are: mechanical, forced flow, and suction lift. Figures 2.1 and 2.2 illustrate forced flow and suction lift sample gathering subsystems, respectively. Figures 2.3 and 2.4 illustrate a mechanical sample gathering subsystem at a weir and flume installation respectively. These subsystems are compared in Table 2.4.

2.3.2.1.3 Sample Transport System

A majority of commercially available composite samplers have fairly small diameter tubing in the sample train which is vulnerable to plugging, due to the buildup of fats, other solids and insoluble components. Adequate flow rates must be maintained throughout the sampling train to effectively transport suspended solids.

To optimize sampler performance and reliability, the following features and procedures are desirable:

- . Use a sample transport line with at least a 6 mm ($\frac{1}{4}$ inch) internal diameter.
- . For most applications, select samplers which minimizes contact of the water/wastewater with metal surfaces during sample transport.
- . For peristaltic pumps, use a sample line which is transparent and flexible, and made of an inert material such as Tygon. For collection of organics, use sample lines constructed of silicone rubber. Do not use silicone rubber transport lines for trace metal sampling since zinc is a major contaminant.(8)
- . Conduct tests on sample transport lines and containers to assure that the sample is not contaminated.
- . Prevent clogging of sample lines by avoiding sharp bends, twists, or kinks.
- . Flush the sample line prior to and immediately after each sample collection. A clean water flush is effective (4) but not feasible in most instances. A complete air purge is sufficient for non-permanent or winter operation.
- . Select a sample pump capable of lifting a sample a vertical distance of 6.1 m (20 feet) and maintaining a line velocity of 0.6 to 3.0 m/sec. (2 to 10 ft/sec.).(7)

PRESSURE OPERATION

Propellant under pressure from a source (A) is metered by a control valve (B) for rate-meter (C) into accumulator tank (D). On reaching a preselected pressure, a pneumatic relay (E) releases the accumulated propellant through inlet line (F) to the sample intake chamber (G). Pressure in the chamber closes its check valve (H) and propels the sample through outlet line (I) and into the sample bottle (J). Excess propellant vents through the sample line, thereby purging it of liquid and incidentally providing protection against line freezing in cold weather. The resulting pressure drop recloses the relay (E) and the sampling cycle repeats at a repetition rate determined by adjusting the control valve (B).

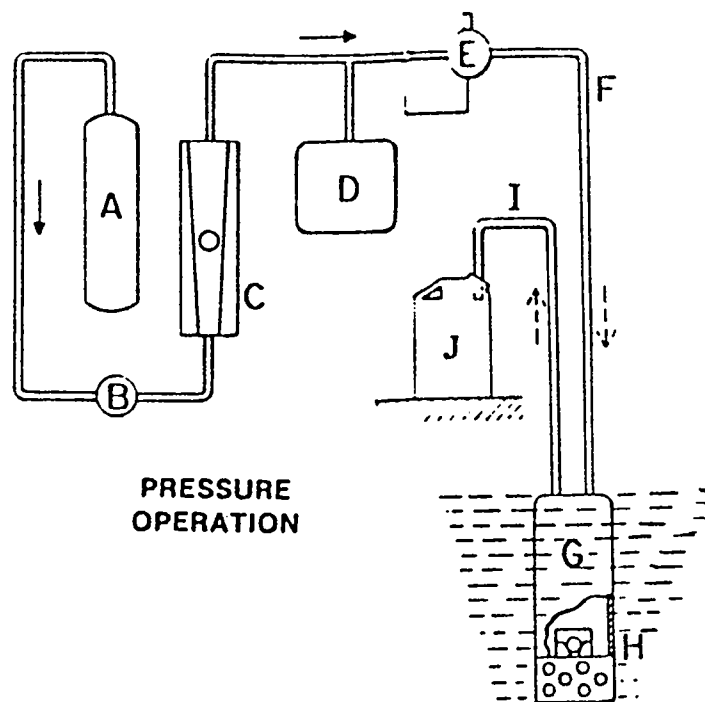


Figure 2.1 Schematic of Forced Flow Type Sampler

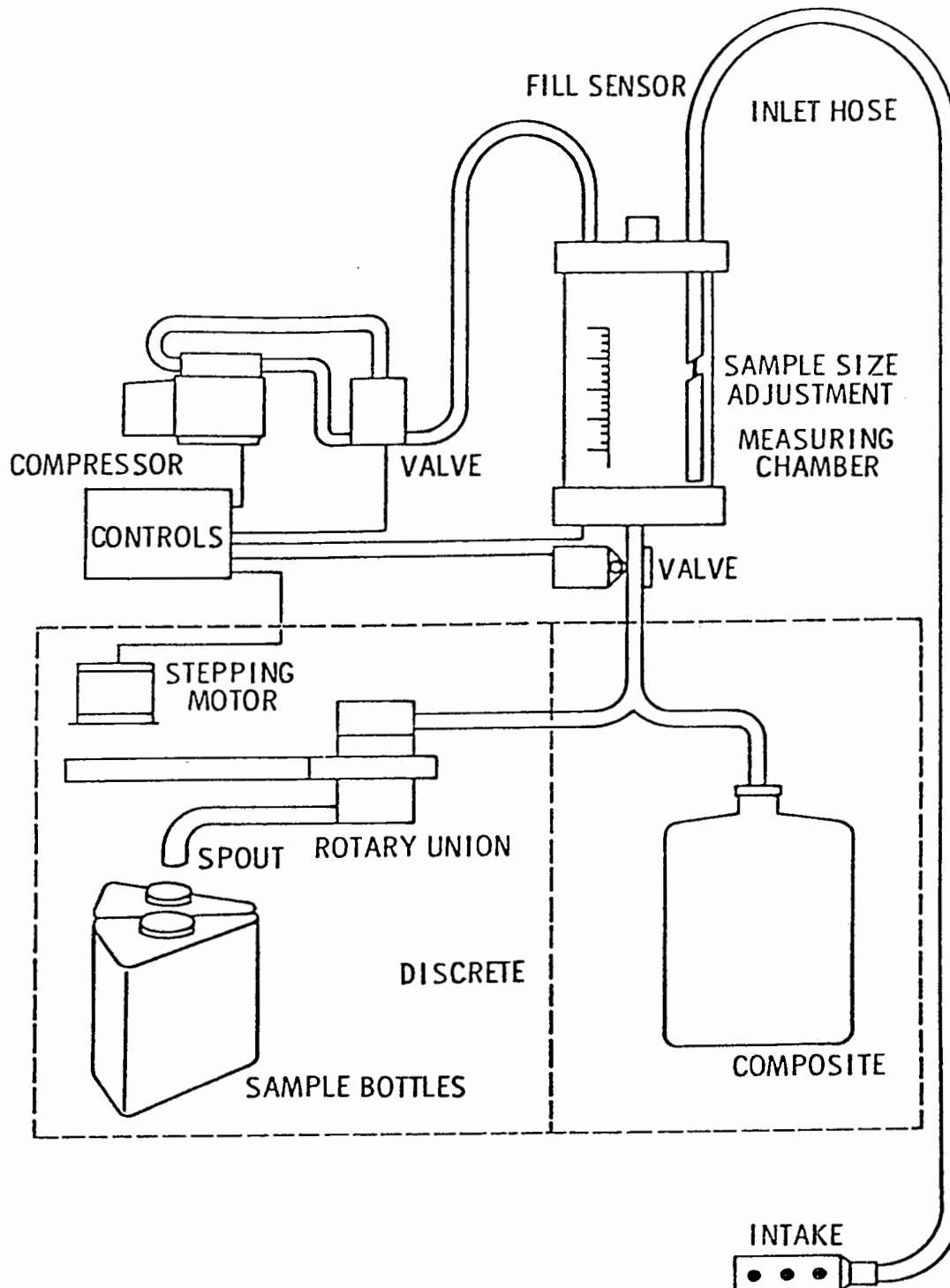


Figure 2.2 Schematic of Suction Lift Type Sampler

Parts List

No.	Description
1.	Motor-Reducer
2.	Drive Sprocket
3.	Driven Sprocket
4.	Roller Chain
5.	Scoop
6.	Scoop Counter Weight(not shown)
7.	Limit Switch
8.	Time Clock
9.	Alum. Sampler Casting
10.	Alum. Sampler Support
11.	Outlet Coupling
12.	Unilet Body & Cover

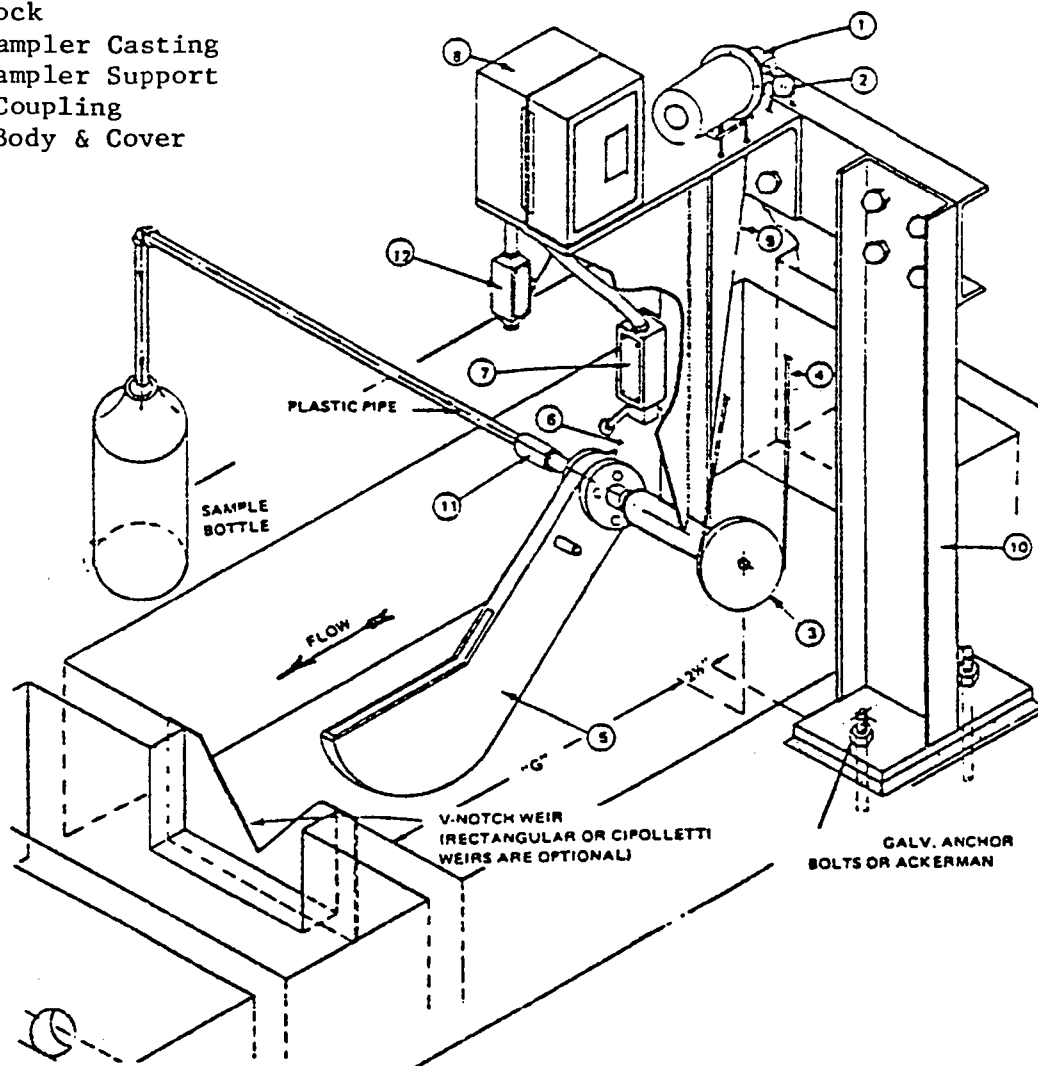


Figure 2.3 Schematic of Mechanical Type Sampler (Weir Installation)

Parts List

No.	Description
1.	Motor - Reducer
2.	Drive Sprocket
3.	Driven Sprocket
4.	Roller Chain
5.	Scoop
6.	Scoop Counter Weight(not shown)
7.	Limit Switch
8.	Time Clock
9.	Alum. Sampler Casting
10.	Alum. Sampler Support
11.	Outlet Coupling
12.	Unilet Body & Cover

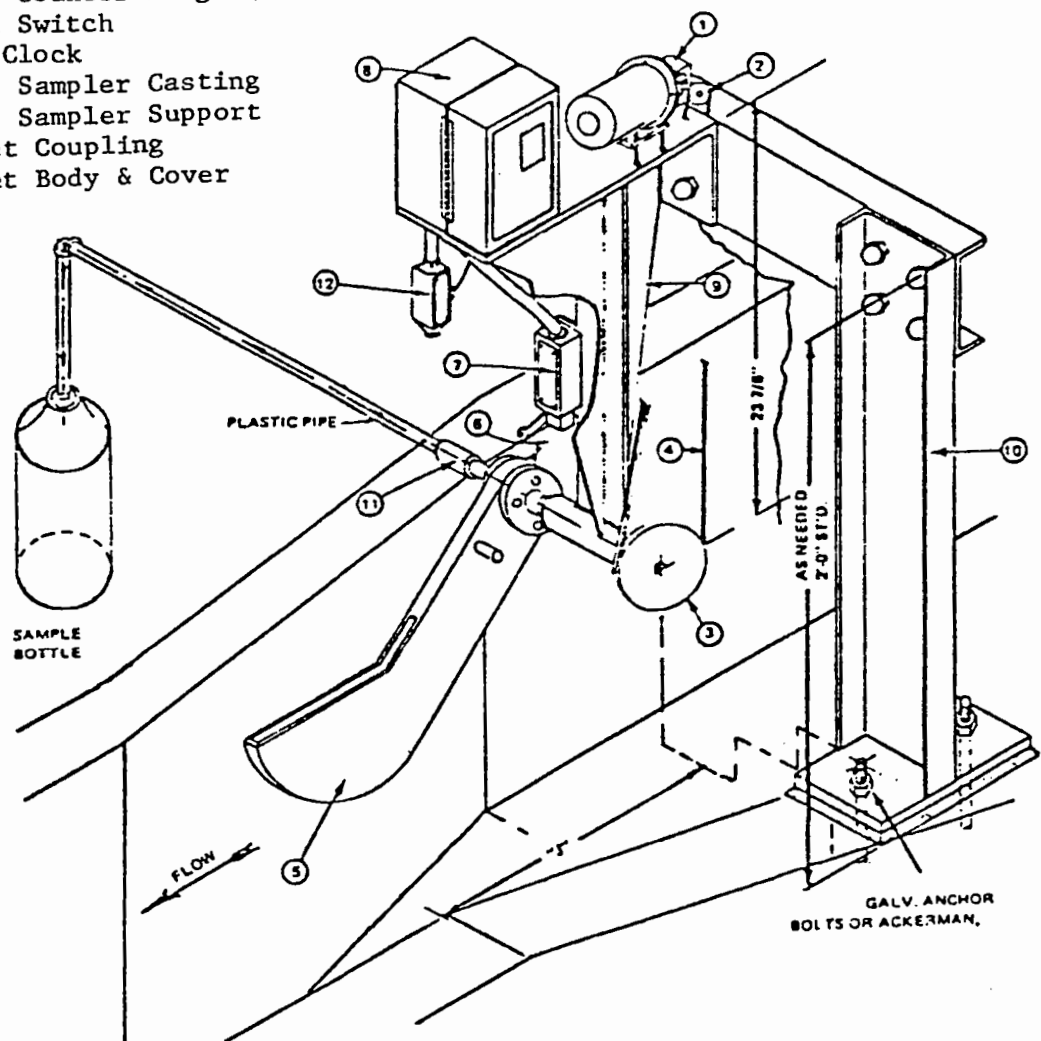


Figure 2.4 Schematic of Mechanical Type Sampler (Flume Installation)

TABLE 2.4 COMPARISON OF SAMPLE GATHERING SUBSYSTEMS

Feature	Mechanical	Forced Flow	Suction Lift
Lift	High	High	Limited to 7.6 m (25 feet) or less
Sample intergration over the entire depth	Possible	Possible with pumps but not with ejection units	Possible with multiple intakes
Obstruction to flow	Significant	Less than mechanical subsystem	Very little
Explosion-proof	Some	Pneumatic ejection units meet this requirement	Some
Dissolved gasses	No problem	No problem	Not suited but if used, the initial flow should be discarded
Fouling	Exposed parts have a tendency to foul	Not easily fouled	Intake tubing of less than 6 mm (1/4") I.D. is prone to fouling
Sample Volume	Suitable for wide range	Pump suitable for wide range Pneumatic ejection units suitable for sample volume	Should be independent of vertical lift
Flexibility	Limited	Moderate	Maximum
Maintenance	Heavy	Moderate but costly	Little

- The importance of line velocity and isokinetic conditions (intake velocity same as velocity of flow of water) depends on the concentration and density of the non-filterable suspended solids in the water, the program requirements for accuracy of suspended solids determinations, and any other parameters affected by suspended solids concentrations. If a program requires maintaining isokinetic conditions, dial adjustment of intake velocity is a desired feature.

- . All materials should be examined to assure that they do not contaminate the sample.

2.3.2.1.4 Sample Storage Subsystem

Discrete samples are subject to considerably more error introduced through sample handling, but provide opportunity for manual flow compositing and time history characterization of a waste stream during short period studies. The desired features of sample storage subsystems are:

- . Flexibility of discrete sample collection with provision for single composite container.
- . Minimum discrete sample container volume of 500 mL (0.13 gal.) and a minimum composite container capacity of 7.57 L (2.0 gal.).
- . Storage capacity of at least 24 discrete samples.
- . Containers of conventional polyethylene or borosilicate glass and of wide mouth construction.
- . Capability for cooling samples by refrigeration or a space for packing ice and maintaining samples at 4° to 6°C (39° to 43°F) for a period of 24 hours at ambient temperature range between -30° to 50°C (-22° to 122°F).
- . Adequate insulation for the sampler to be used in either warm or freezing ambient conditions.

2.3.2.1.5 Controls and Power Subsystem

The following are desired power and controls features which may be necessary depending upon whether the sampler is to be portable or a permanent installation:

- . Capability for either AC (Electrically grounded system) or DC operation.
- . Battery life for two to three days of reliable hourly sampling without recharging.
- . Battery weight of less than 9 kg (20 lb.) and sealed so no leakage occurs.
- . Solid state logic and printed circuit boards.
- . Timing and control systems contained in a waterproof compartment and protected from humidity. Timer should use solid state logic and a crystal controlled oscillator.
- . Controls directly linked to a flow meter to allow both flow-proportional sampling and periodic sampling at an adjustable interval from 10 minutes to 4 hours.
- . Capability of multiplexing, that is, drawing more than one sample into a discrete sample bottle to allow a small composite over a short interval. Also capability for filling more than one bottle with the same aliquot for addition of different preservatives.
- . Capability of adjusting sample size and ease in doing so.

2.3.2.1.6 General Desirable Features

For safety, maintenance, reliability and security in field applications, the following general features are desired in an automatic sampler:

- . Water tight casing to withstand total immersion and high humidity.
- . Vandal proof casing with provisions for locking.
- . A secure harness or mounting device if sampler is placed in a sewer.
- . Explosion proof construction.
- . Sized to fit in a standard manhole without disassembly.
- . Compact and portable for one-man installation.
- . Overall construction, including casing, of materials resistant to corrosion (plastics, fiberglass, stainless steel).
- . Exterior surface painted a light color to reflect sunlight.
- . Low cost, availability of spare parts, warranty, ease of maintenance, reliability and ruggedness of construction.

2.3.2.2 Installation and Use

2.3.2.2.1 General Consideration

Sampling equipment will yield good results only when properly installed and maintained. A few general guidelines follow:

- . When a sampler is installed in a manhole, secure it either in the manhole, for instance, to a rung above the high water line or outside the manhole to an above ground stake by means of a rope.
- . Place the intake tubing vertically or at such a slope to ensure gravity drainage of the tubing between samples, avoiding loops or dips in the line.
- . Clean sample bottles, tubing and any portion of the sampler which contacts the sample between setups. Whatever methods of cleaning are used, all parts of the sampler which come in contact with the sample should be rinsed with tap water and then given a final rinse with distilled water. A distilled water rinse may not be necessary between setups on the same waste stream.
- . Inspect the intake after each setup and clean, if necessary. Exercise care when placing the intake(s) in a stream containing suspended solids and run the first part of the sample to waste. Maintain sufficient velocity of flow at all times to prevent deposition of solids. When a single intake is to be used in a channel, place it at six-tenths depth (point of average velocity). (10)(11) For wide or deep channels where stratification exists, set up a sampling grid as shown in section 8.4.
- . Maintain electrical and mechanical parts according to the manufacturer's instructions. Replace the desiccant as needed. If a wet-cell lead-acid battery is used, neutralize and clean

- up any spilled acid.
- . Position the intake in the stream facing upstream. Limit the orientation of the intake 20 degrees on either side of the head-on. Secure the intake by a rope at all times with no drag placed on the inlet tubing.
- . After the installation is complete, collect a trial sample to assure proper operation and sample collection. The sampler must give replicate samples of equal volume throughout the flow range. If the sampler imposes a reduced pressure on a waste stream containing suspended solids, run the first part of the sample to waste.

2.3.2.2.2 Winter Operation

For outdoor use in freezing temperatures, use special precautions to prevent the collected sample(s) from freezing. These include:

- . Place the sampler below the freezing level or in an insulated box.
- . When AC is available, use a light bulb or heating tape to warm sampler. When installation below the freezing level is not possible and line current is available wrap 1.2 to 1.8 m (4 to 6 ft.) heat tapes (thermostatically protected 3°C (38°F)) around the sample bottle and the intake lines. Loosely wrap a large 10 mL plastic trash bag over the heat tape on the intake lines. Place a large plastic bag over the sampler as loosely as possible.(7)
- . Place the line vertically or at such a slope to ensure gravity drainage back to the source. Even with a back-purge system, some liquid will remain in the line unless gravity drainage is provided. If an excess length of tubing exists, cut it off. Keep all lines as short as possible.
- . Do not use catalytic burners to prevent freezing since vapors can affect sample composition. When power is unavailable, use a well insulated box containing the sampler, a battery and small light bulb to prevent freezing.

2.3.2.3 Selection of an Automatic Sampler

To choose an automatic sampler, list the desired features needed for a particular sampling program and select the sampler that best fits the requirements consistent with the sampling objectives.

The following is a list of features to be considered in selecting an automatic sampler:

1. Vertical lift
2. Submergence
3. Explosion proof
4. Intake tube: diameter/material
5. Dissolved gases
6. Suspended solids

7. Oils and grease and floating material
8. Materials - Organic pollutants
9. Isokinetic sampling
10. Sample type: continuous, composite: time proportional, flow proportional, and so on.
11. Multiple intakes
12. Multiplexing
13. Dependability
14. Ease of operation
15. Maintenance
16. Availability

2.4 TYPE OF SAMPLE

The type of sample collected depends on the variability of flow, variability of water or wastewater quality, the accuracy required and the availability of funds for conducting the sampling and analytical programs.

2.4.1 Grab Sample

A grab sample is defined as an individual discrete sample collected over a period of time not exceeding 15 minutes. It can be taken manually, using a pump, scoop, vacuum, or other suitable device. The collection of a grab sample is appropriate when it is desired to:

1. Characterize water quality at a particular time.
2. Provide information about minimum and maximum concentrations.
3. Allow collection of variable sample volume.
4. Corroborate composite samples.
5. Meet a requirement of a discharge permit.

2.4.2 Composite Sample

A composite sample is defined as a sample formed by mixing discrete samples taken at periodic points in time or a continuous proportion of the flow. The number of discrete samples which make up the composite depends upon the variability of pollutant concentration and flow. A sequential composite is defined as a series of periodic grab samples each of which is held in an individual container, then composited to cover a longer time period. Six methods are used for compositing samples. Table 2.5 lists those methods with their advantages and disadvantages. Choice of composite type is dependent on the program and relative advantages and disadvantages of each composite type.

2.4.3 Selection of Sample Type

Use grab samples when: (12)(13)(14)

1. The stream does not flow continuously such as batch dumps.
2. The water or waste characteristics are relatively constant.
3. The parameters to be analyzed are likely to change with storage such

TABLE 2.5 COMPOSITING METHODS

Sample mode	Compositing Principle	Advantages	Disadvantages	Comments
Continuous	Constant pumping rate	Minimal manual effort, requires no flow measure- ment	Requires large sample capacity; may lack represen- tativeness for highly variable flows	Practical but not widely used
Continuous	Sample pumping rate proportional to stream flow	Most representa- tive especially for highly vari- able flows; minimal manual effort	Requires accurate flow measurement equipment, large sample volume, variable pumping capacity, and power	Not widely used
Periodic	Constant sample volume, constant time interval between samples	Minimal instru- mentation and manual effort; requires no flow measurement	May lack represen- tativeness espe- cially for highly variable flows	Widely used in both automatic samplers and manual sampling
Periodic	Constant sample volume, time interval between samples propor- tional to stream flow	Minimal manual effort	Requires accurate flow measurement/ reading equipment Manual compositing from flow chart	Widely used in automatic as well as manual sampling

(Continued)

TABLE 2.5 (Continued)

Sample	Compositing principle	Advantages	Disadvantages	Comments
Periodic	Constant time interval between samples, sample volume proportional to total stream flow since last sample	Minimal instrumentation	Manual compositing from flow chart In absence of prior information on the ratio of minimum to maximum flow, there is a chance of collecting either too small or too large individual discrete samples for a given composite volume	Not widely used in automatic samplers but may be done manually
Periodic	Constant time interval between samples, sample volume proportional to total stream flow at time of sampling	Minimal instrumentation	Manual compositing from flow chart In absence of prior information on the ratio of minimum to maximum flow, there is a chance of collecting either too small or too large individual discrete samples for a given composite volume	Used in automatic samplers and widely used as manual method

- as dissolved gases, residual chlorine, soluble sulfide, oil and grease, microbiological parameters, organics, and pH.
4. Information on maximum, minimum or variability is desired.
 5. The history of water quality is to be established based on relatively short time intervals.
 6. The spatial parameter variability is to be determined, for example, the parameter variability throughout the cross section and/or depth of a stream or large body of water.

Use composite samples when:

1. Determining average concentrations.
2. Calculating mass/unit time loading.

2.4.4 Method of Manual Compositing

When using a constant volume/time proportional compositing method, use previous flow records to determine an appropriate flow volume increment so a representative sample is obtained without exceeding the bottle capacity or supply.

The preparation of the flow rated composite is performed in various ways. Table 2.6 summarizes the techniques necessary for preparing composites from time constant/variable volume samples.

2.4.5 Examples of Manual Compositing

Example 2.1 illustrates the method of manual compositing for time constant/volume proportional to discharge since last sample, when records of totalized flow are available.

Example 2.2 illustrates the method of manual compositing for time constant/volume proportional to discharge since last sample, when records of flow rates are available.

Example 2.3 illustrates the method of manual compositing for time constant/volume proportional to instantaneous flow rate.

Example 2.4 illustrates the method of manual compositing for the constant volume/time proportional to equal increment discharge passing the sampling point, based on the past records of totalized flow.

Example 2.5 illustrates the method of manual compositing for the constant volume/time proportional to equal increment discharge passing the sampling point, based on the past records of flow rates.

Example 2.1: Manually preparing a composite sample using the method, time constant/volume proportional to discharge since last sample.

Given: A 500 mL discrete sample was taken at the end of each hour over an eight hour shift. A 3,000 mL composite is desired. A recording of totalized flow is available.

TABLE 2.6 MANUAL PREPARATION OF VARIABLE VOLUME COMPOSITE

Type	Preparation	Equation
Time constant/proportional to total flow	Determine volume since last sample by integration	$a_i = \frac{\Delta Q_i}{\Sigma \Delta Q_i} V_c$
		a_i = aliquot volume to be extracted from ith discrete sample
		V_c = composite volume (known)
		q_i = flow rate when ith discrete sample was taken (from flow record)
		Q_i = flow volume when ith discrete sample was taken
		Q_{i-1} = flow volume when ith -1 discrete sample was taken
		ΔQ_i = flow volume or rate since last sample (integration)
Time constant/volume proportional to instantaneous flow	Note flow rate at each time of discrete sample collection	$\Sigma \Delta Q_i$ = total flow volume (estimated)
		$a_i = \frac{q_i}{n} V_c$
		where: a_i = aliquot volume to be extracted from ith discrete sample
		q_i = flow rate when ith discrete sample was taken (from flow record)
		V_c = composite sample volume
		n = number of discrete samples

Sample No.	Q_i	ΔQ_i	a_i	a_i (adjusted) = $a_i (500/\max a_i)$
(i)	(liters)	(liters)	(mL)	(mL)
0	0	-	-	-
1	858	858	100	77
2	3,462	2,604	303	232
3	8,462	4,792	558	427
4	12,347	4,093	477	365
5	17,950	5,603	653	500
6	21,225	3,275	382	292
7	24,600	3,375	393	301
8	<u>25,750</u>	<u>1,150</u>	<u>134</u>	<u>103</u>
		$\Sigma \Delta Q_i = 25,750$	$\Sigma a_i = 3,000$	2,297

$\max a_i = 653 \text{ mL}$

Steps:

1. Enter Q_i from the record and calculate $Q_i = Q_i - Q_{i-1}$
2. Calculate $a_i = \frac{V_c}{\Sigma \Delta Q_i} (\Delta Q_i)$, where $V_c = 3000 \text{ mL}$
3. Check to see if maximum a_i exceeds discrete sample volume, that is $653 \text{ mL} > 500 \text{ mL}$.
4. If it does, adjust aliquot sizes using the relationship:

$$a_i \text{ (adjusted)} = a_i \left[\frac{\text{discrete sample volume}}{\max a_i} \right] = \frac{500}{653} = 0.77$$
5. Determine the adjusted composite volume from a_i (adjusted). This example illustrates that although desired composite volume was $3,000 \text{ mL}$ (V_c) because of discrete sample volume size, only $2,297 \text{ mL}$ of composite sample can be obtained.

Example 2.2 Manually preparing a composite sample using the method, time constant/volume proportional to discharge since last sample.

Given: A 500 mL discrete sample was taken at the end of each hour over an 8 hour shift. A $3,000 \text{ mL}$ composite is desired. A recording of flow rate is available.

Sample No. (i)	q_i (liters) sec.	ΔQ_i (liters) sec.	a_i (mL)	a_i (adjusted) = a_i (500/max a_i) (mL)
0	961	-	-	-
1	2,025	1,483	146	132
2	3,700	2,862	282	255
3	5,212	4,456	439	397
4	6,004	5,608	553	500
5	5,018	5,511	543	491
6	4,002	4,510	444	401
7	3,089	3,546	349	316
8	1,847	2,468	244	221
		$\Sigma \Delta Q_i = 30,444$	$\Sigma a_i = 3,000$	2,713

Max $a_i = 553$ mL

Steps:

1. Enter q_i from record and use trapezoidal rule to calculate $(\Delta Q_i = q_i + q_{i-1})/2$ (another integration scheme could be used if warranted).
2. Calculate $a_i = \frac{V_c}{\Sigma \Delta Q_i} (\Delta Q_i)$ where $V_c = 3,000$ mL
3. Check to see if maximum a_i exceeds discrete sample volume
4. If it does, adjust aliquot sizes using the relationship:

$$a_i \text{ (adjusted)} = a_i \left[\frac{\text{discrete sample volume}}{\max a_i} \right]$$
5. Determine the adjusted composite volume from a_i (adjusted). This example illustrates that although desired composite volume was 3,000 mL (V_c) because of discrete sample volume size, only 2,713 mL of composite sample can be obtained.

Example 2.3: Manually preparing a composite sample using the method, time constant/volume proportional to instantaneous flow rate.

Given: 500 mL discrete samples were taken at hourly intervals over an

eight hour shift. A 2,000 mL composite is desired. A recording of flow rate is available.

Sample No. (i)	q_i (liters) Sec.	a_i (mL)	a_i (adjusted) = $a_i \times 500/\max a_i$ (mL)
1	600	109	107
2	1,000	182	179
3	1,700	309	304
4	2,800	509	500
5	1,800	327	321
6	1,400	255	250
7	1,000	182	179
8	700	127	125

$$\Sigma q_i = 11,000$$

$$\Sigma a_i = 2,000$$

$$1,965$$

$$\max a_i = 509 \text{ mL}$$

Steps:

1. Enter q_i from record and sum.
2. Calculate $a_i = q_i V_c / q_i$
3. Check to see if maximum a_i ($500/509$) = a_i (adjusted). This example illustrates that with an individual discrete sample capacity of 500 mL only 1,965 mL volume of composite sample can be obtained. If it is desired to collect a composite sample of 3,000 mL volume, obviously larger sized (750 mL) capacity bottles or greater sampling frequency will be required for collecting individual discrete samples.

Example 2.4 Manually preparing a composite sample using the method, constant volume/time proportional to equal increment discharge.

Given: A 500 mL discrete sample was taken each time an average hourly flow flowed past the sample point. Sampling period is eight hours.

In addition, a 500 mL sample was taken at the end of the sampling period. A composite of 4,000 mL is desired. A recording of total flow from past record is available.

Period ith hour	<u>Past Record</u>		<u>Actual</u>		a_i (mL)	Sample No.
	Q_i (past) (liters)	ΔQ_i (past) (liters)	Q_i (actual) (liters)	ΔQ_i (actual) (liters)		
0	0	0	0	0		
1	868	868	797	797	500	1
2	4,024	3,156	3,648	2,851	500	2
3	7,616	3,592	8,002	4,354	500	3
4	11,453	3,837	11,709	3,707	500	4
5	16,629	5,176	16,056	4,347	500	5
6	20,377	3,748	19,763	3,707	500	6
7	22,625	2,248	24,321	4,558	500	7
8	25,000	<u>2,375</u>	26,650	<u>2,229</u>	<u>264</u>	8
	$\Sigma \Delta Q_i$ (past) = 25,000		$\Sigma \Delta Q_i$ (actual) = 26,650			9

Steps:

1. Enter Q_i from past record and calculate $\Delta Q_i = Q_i - Q_{i-1}$.
2. Determine the number of samples from the overall sampling period. On the basis of the number of samples required for the overall sampling period, P , determine the average flow from the past records for the time interval, T , between the successive discrete samples. In our case, the number of samples for the sampling period = 8. Overall sampling period, $P = 8$ hours.

$$\text{Time interval, } T = \frac{8 \text{ hours}}{8} = 1 \text{ hour}$$

Average flow for the time interval between successive samples

$$\text{from past} = \frac{\Sigma Q_i \text{ (past)}}{P} = \frac{25,000}{8} = 3,125 \text{ L.}$$

3. Aliquot size $a_i = 500$ mL
4. Collect each discrete sample every time 3,125 L passes the sampling point; and an additional one 500 mL sample aliquot at the end of the sampling period.
5. Record the actual flow.

6. Note the total flow for the sampling period. In our case it is $\Sigma \Delta Q_i$ (actual) = 26,650 L.
7. Calculate the difference between $\Sigma \Delta Q_i$ (actual) and $\Sigma \Delta Q_i$ (past) which is $26,650 - 25,000 = 1,650$ L. This is the flow which passes the sampling point after taking the last sample for equal incremental discharge, up to the end of sampling. This flow is sampled by the sample taken at the end of the sampling period.
8. Compute the representative aliquot required for the unbalanced flow in step 7 in proportion to the equal increment flow.
 Required aliquot volume =
$$\frac{\Sigma \Delta Q_i(\text{actual}) - \Sigma \Delta Q_i(\text{past})}{\text{equal increment discharge volume}} (a_i)$$

$$= \frac{26,650 \text{ L} - 25,000 \text{ L}}{3,125 \text{ L}} (500 \text{ mL}) = 264 \text{ mL}$$
9. Composite volume: = $\Sigma a_i = 8$ aliquots of 500 mL + 264 mL from the aliquot taken at the end of the sampling period for a total of 4,264 mL.

Example 2.5 Manually preparing a composite sample for constant volume/time proportional to equal increment discharge.

Given: A 500 mL discrete sample was taken each time an average hourly flow flowed past the sample point. Sampling period is eight hours. In addition, a 500 mL sample was taken at the end of the sampling period. A composite of 4,000 mL is desired. A recording of instantaneous flow rate from past records is available.

Period ith hr.	Q_i (past) (liters)	ΔQ_i (past) (liters)	Q_i (actual) (liters)	ΔQ_i (actual) (liters)	a_i (mL)	Sample No.
0	40	-	30	-	-	-
1	60	50	50	40	-	-
2	100	80	110	80	500	1
3	120	110	110	110	500	2
4	160	140	150	130	500	3
5	160	160	180	165	500	4
6	150	155	180	180	500	5
7	110	130	110	145	500	6
8	100	105	90	100	500	7
					86	8
						9
		$\Sigma \Delta Q_i$ (past) = 930		$\Sigma \Delta Q_i$ (actual) = 950		

Steps:

1. Enter Q_i from past record and use trapezoidal rules to calculate $\Delta Q_i = (Q_i + Q_{i-1})/2$ (another integration scheme could be used if warranted).
2. Determine the number of samples for the overall sampling period. On the basis of number of samples required for the overall sampling period, P , determine the average flow from the past records for the time interval, T , between the successive discrete samples. In our case the number of samples for the sampling period = 8. Overall sampling period, $P = 8$ hours

$$\text{Time interval, } T = \frac{8 \text{ hours}}{8} = 1 \text{ hour.}$$

Average flow for the time interval between successive samples from

$$\text{past records} = \frac{\Sigma \Delta Q_i}{P} = \frac{930}{8} = 116 \text{ L}$$

3. Aliquot size $a_i = 500$ mL.
4. Collect a discrete sample each time 116 liters passes the sampling point and one additional aliquot of 500 mL at the end of the sampling period.
5. Record the actual flows per unit of time interval selected. For example; hours, minutes, days.

6. Calculate the total actual flow for the the sampling period. In our case it is $\Sigma \Delta Q_i$ (actual) = 950 L.
7. Calculate the difference between $\Sigma \Delta Q_i$ (actual) and $\Sigma \Delta Q_i$ (past) which is $950 - 930 = 20$ L. This is the flow which passes the sampling point after taking the last sample for equal incremental discharge, up to the end of the sampling period.
8. Compute the representative aliquot required for the unbalanced flow determined in step 7 in proportion to the equal increments.

$$\text{Required aliquot volume} = \frac{\Sigma \Delta Q_i \text{ (actual)} - \Sigma \Delta Q_i \text{ (past)}}{\text{equal increment discharge volume}} (a_i) = \frac{(20 \text{ L})(500 \text{ mL})}{116 \text{ L}} = 86 \text{ mL}$$

9. Composite volume = $\Sigma a_i = 8$ aliquots of 500 mL + 86 mL from the aliquot taken at the end of the sampling period = 4,086 mL.

2.5 PLANNING A SAMPLING PROGRAM

The following considerations can help to plan an appropriate sampling program. The planning process can be divided into four stages: preliminary plan, evaluation of preliminary plan, final plan, and program evaluation.

2.5.1 Preliminary Plan

In this stage, emphasis is on the collection of preliminary information on the entity to be sampled, the sampling sites and the flow characteristics. This information may be available from records of previous surveys. Where such information is not available, carry out a reconnaissance survey to become thoroughly familiar with actual site conditions. Table 2.7 shows the type of information needed in most cases. Collect the appropriate information for Table 2.7 and based on this information, draw up a preliminary sampling plan. Delineate preliminary sampling objectives and details of the plan such as anticipated parameters, sample type, sample size, and frequency, specified. Record this information in a tabular form similar to Table 2.8.

Make an estimate of the resources (manpower and equipment) needed for the sampling program. Table 2.9 illustrates one form for keeping records of available resources and estimated needs of a sampling program. Include into the preliminary sampling plan, sample preservation and chain of custody procedures.

TABLE 2.7 PRESURVEY INFORMATION

<u>Entity</u>		<u>Process Details</u>	
_____	Treatment Plant ()	1.	_____
_____	Industry ()	2.	_____
_____	River ()	3.	_____
_____	Estuary ()	4.	_____
_____	Sewer ()	5.	_____
_____	Water Mains ()	6.	_____

<u>Plans:</u>	<u>Yes</u>	<u>No</u>	<u>Waste sources</u>	<u>Flows</u>
Sewer maps	()	()	1. _____	_____ P/C
Water line net-work maps	()	()	2. _____	_____ P/C
River and tribu-tary maps	()	()	3. _____	_____ P/C
Treatment plant maps	()	()	4. _____	_____ P/C
Estuary zone maps	()	()	5. _____	_____ P/C

<u>Channel</u>	<u>Flow Variability</u>	<u>Manholes ()</u>
Width _____	Hourly Max _____	other _____
Depth _____	Hourly Min _____	Diameter or width _____
	Hourly Average _____	Depth _____

<u>Pipe</u>	
Diameter _____	Daily Max _____
Material _____	Daily Min _____
	Daily Average _____

P = pipe flow C = open channel flow

(continued)

TABLE 2.7 (Continued)

<u>Topography</u>	<u>Physical Characteristics of Flow</u>	<u>Safety</u>	<u>Security</u>
Level ()	Odor _____	Steep banks ()	Fence ()
Slopes ()	Temperature _____	Soft grounds ()	Open ()
Vegetation ()	Oil & Grease _____	Gases ()	Guarded ()
		specify _____	
Swamp ()	Clear () Turbid ()	<u>Stream Currents</u>	Lighted ()
Other () Specify _____	Suspended Solids concentration _____	Turbulent ()	Other () Specify _____
		Sluggish ()	_____

Sampling Sites

Distance:	Numbers:	Accessibility:	Convenience:
Near ()	Few ()	Road ()	Sheltered ()
Remote ()	Many ()	Bridge ()	Power available ()
		Other () Specify _____	Other () Specify _____

Additional Information

TABLE 2.8 DETAILS OF SAMPLING

Parameters of Interest	Sample Type	Sample Frequency	Number of Samples	Field or Lab Analysis	Sample Volume	Preservation	Holding Times	Analytical Methods	Chain of Custody Procedure	Remarks

TABLE 2.9 MANPOWER AND EQUIPMENT FOR A SAMPLING PROGRAM

<u>Manpower:</u>	<u>Available</u>	<u>Needed</u>
------------------	------------------	---------------

Sampling Program Coordinator		
Quality Assurance Coordinator		
Laboratory Custodian		
Field Sampling Crew Chief		
Field Laboratory Crew		
Shipment Truck Driver		
Others		

Equipment:

Automatics Samplers:

Type

Manual Samplers:

Type

Flow Meters:

Type and Size

(Continued)

TABLE 2.9 (Continued)

	Available	Needed
Portable Weirs:		
Portable Flumes:		
<u>Sounding Equipment:</u>		
Wading rods		
Cable lines		
Sounding rods		
Sounding Weight:		
<u>Boats:</u>		
<u>Trucks:</u>		

(Continued)

TABLE 2.9 (Continued)

	Available	Needed
<u>Field Laboratory:</u>		
<u>Other Equipment:</u>		

2.5.2 Evaluation of Preliminary Plan

Circulate the preliminary sampling plan among other divisions (laboratory, field personnel, and quality assurance branch) connected with the sampling program for their considerations and further deliberations before drawing up a final sampling program.

2.5.3 Final Plan

Base the final sampling plan on the preliminary plan and subsequent deliberations and coordination with the personnel involved. Spell out the final plan in detail including: objectives, sampling locations, number and frequency of samples, sample types, quality assurance samples (field spikes, replicates, etc.), preservation and chain of custody procedures, designation of authorities, field procedures and other pertinent information so that the sampling plan can be executed in an efficient and well coordinated manner. Pre-sampling briefing should be a key element in any sampling program.

2.5.4 Program Evaluation

Evaluate the entire program after the samples are collected and analyzed to determine the effectiveness of the final plan and to avoid future pitfalls and problems. The performance evaluation should enhance the efficiency of the program and quality of the data generated from a sampling program.

2.6 FIELD PROCEDURES

The heart of the sampling program is field operations. If proper precautions and care are not exercised in the field procedures, the entire sampling program will become meaningless despite adequate planning, analytical facilities, and personnel. The key to the success of a field sampling program lies in good housekeeping, collection of representative samples, proper handling and preservation of samples, and appropriate chain of custody procedures.

2.6.1 Good Housekeeping

1. Compose written instructions on field sampling procedures.
2. Prior to use, check sampling equipment to insure good operating conditions and cleanliness. Keep the equipment ready to be used. After the sampling has been completed, clean the equipment and keep it in neat environments. Follow manufacturer's specifications in carrying out routine maintenance of the equipment.
3. Check primary (e.g. flume) and secondary (e.g. Recorder/transmitter) devices for the following:
 - a. Locations
 - . At the appropriate place as defined in sampling program.
 - . Upstream and downstream conditions meet the requirement of specific installation of primary and secondary devices.
 - b. Dimensions of primary devices such as flumes, weirs, and still wells to be sure they are within tolerance limits.
 - c. General conditions of channel, primary and secondary devices and stilling wells. Note any unusual wear, debris in channel or distortion of chart paper.
 - d. Calibration of primary and secondary devices before actual measurements of flow are taken.
4. Check all sample bottles to avoid contamination. Clean the bottles as indicated in Section 17.2.5 and 17.2.6. If this cannot be done, do not collect the sample.
5. In the laboratory, clean the sample intake tubing by flushing with hot water and then rinsing with distilled water. In the field, rinse several times with sample water.
6. Maintain record of breakdowns in the sampling operations, the problems encountered with different equipment and how they were resolved. This information indicates the reliability of the equipment, the problem areas that need to be brought to the manufacturer's attention, and considerations for future procurements.
7. Hold training sessions for field sampling teams.

2.6.2 Guidelines for Representative Sample

To obtain representative samples, follow these guidelines:

1. Collect the sample where water is well mixed, that is near a Parshall flume or at a point of hydraulic turbulence such as downstream of a hydraulic jump. Certain types of weirs and flumes tend to enhance the settling of solids upstream and accumulate floating solids and oil downstream, therefore such locations should be avoided as a sample source. For low level turbulence, mechanical or air mixing should be used to induce turbulence except when dissolved gases or volatile materials are being sampled.
2. Collect the sample in the center of the channel at 0.4 to 0.6 depth from the bottom where the velocity of flow is average or higher than average and chances of solids settling is minimum. This depth avoids bottom bed loads and top floating materials such as oils and grease.
3. In a wide channel, divide the channel cross section into different vertical sections so that each section is equal width. Take a representative sample in each vertical section.
4. In a deep stream or lake, collect the samples at different depths. In those cases of wide and deep streams the samples can be composited or analyzed individually depending upon the program objective.
5. When manual sampling with jars, place the mouth of the collecting container below the water surface and facing flow to avoid an excess of floating material. Keep the hand away from the mouth of the jar as far as possible.
7. Additional guidelines for manual sampling:
 - . Sample facing upstream to avoid contamination.
 - . Force sampling vessel through the entire cross section of the stream wherever possible.
 - . Drop an inverted bucket and jerk line just before impact with the water surface.
 - . Be certain that the sampler closes and opens at the proper time when sampling with a depth integrating sampler; with a point sampler, be certain that sampler opens at a proper depth. If a doubt exists, discard the sample and re-sample.
8. When sampling, it is necessary to fill the bottles completely if the samples are to be analyzed for volatile organics, O_2 , CO_2 , NH_3 , H_2S , free chlorine, pH, hardness, SO_2 , NH_4 , Fe^{++} , oil and grease, acidity or alkalinity. When sampling for bacteria or suspended solids, it is necessary to leave an airspace in the sample container to allow mixing before subsampling.
9. Collect sufficient volume to allow duplicate analyses and quality assurance testing (split or spiked samples). The required sample volume is a summation of that required for each parameter of interest. Refer to USEPA's Methods for Chemical Analyses for Water

and Wastewater, 1979, EPA 600/4-79-0202 for the volume required for analysis of a specific parameter (8), or the laboratory director for minimum volumes to be collected.

10. Maintain an up-to-date log book which notes possible interferences, environmental conditions and problem areas.
11. Since mathematical relationship between volumetric flow and height (or depth) of flow is nonlinear, composite flow proportional samples in relation to the total volume of flow as opposed to gauge height or raw measurement of a secondary device.
12. If samples are taken from a closed conduit via a valve or faucet arrangement, allow sufficient flushing time to insure that the sample is representative of the supply, taking into account the diameter, length of the pipe to be flushed and the velocity of the flow.

2.6.3 Sample Preservation, Handling and Chain of Custody Procedures

When immediate analysis of the collected sample is not possible, take precautions so that the sample characteristics are not altered. Follow these guidelines for sample handling and preservation:

1. Minimize the number of people handling the sample.
2. Follow the guidelines given in chapters 15 and 17 on chain of custody procedures and sample handling.
3. Store the sample in a manner which insures that the parameters to be analyzed are not altered, and use the preservation methods and holding times pertinent to the parameters shown in chapter 17.
4. Insure that the container material does not interfere with the analysis of the specific parameters. Refer to EPA's Methods for Chemical Analyses for Water and Wastewaters, 1979. EPA 600/4-79-020.(8)

2.6.4 Field Analysis and Procedures

The sampling program should specify the various analyses to be performed in the field and the corresponding analytical methods. Field laboratories must also have standard procedures and methods for handling and analyzing samples such that identification, integrity and representativeness of the samples are maintained at all times.

2.7 REFERENCES

1. Water Monitoring Task Force. R.L. Crim, editor, Model State Water Monitoring Program. U.S. Environmental Protection Agency, Office of Water and Hazardous Materials, Washington, D.C., EPA-440/9-74-002.
2. Black, H.H. Procedures for Sampling and Measuring Industrial Wastes. Sewage and Industrial Wastes, 24, pp. 45-65, January 1952.

3. Lauch, R.P. A Survey of Commercially Available Automatic Wastewater Samplers. Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio. Available through National Technical Information Service, Springfield, Virginia 22161. EPA 600/4-76-051, September 1976, PB 241085/AS.
4. Shelley, P.E. and G.A. Kirkpatrick. An assessment of Automatic Sewer Flow Sample. Prepared for the Office of Research and Monitoring, U.S. Environmental Protection Agency, Washington, D.C. 20460, EPA R2-76-261 June 1973.
5. Shelley, P.E. and G.A. Kirkpatrick. An Assessment of Automatic Sewer Flow Sampler. Prepared for the Office of Research and Monitoring, U.S. Environmental Protection Agency, EPA 600/2-76-065 Washington, D.C., December 1975.
6. Shelley, P.E. Design and Testing of a Prototype Automatic Sewer Sampling System. Prepared for the Office of Research and Monitoring, U.S. Environmental Protection Agency, EPA 600/2-76-006, Washington, D.C., March 1976.
7. Harris, E.J. and W.J. Keffer. Wastewater Sampling Methodologies and Flow Measurement Techniques. USEPA Region VII, EPA 907/9-74-005, Kansas City, Missouri, June 1974.
8. Segar, E.A. and A.A. Berberian. Contamination by Oceanographic Samplers. Analytical Methods in Oceanography, American Chemical Society, 1975.
9. U.S. Environmental Protection Agency. National Field Investigation Center, Denver. Comparison of Manual (Grab) and Vacuum Type Automatic Sampling Techniques on an Individual and Composite Basis. EPA 330/1-74-001.
10. Metcalf and Eddy Inc. Wastewater Engineering: Collection, Treatment, Disposal. New York, McGraw-Hill Book Company, 1972, p. 710.
11. Water Measurement Manual. U.S. Bureau of Reclamation. U.S. Government Printing Office, Washington, D.C. 1967. p. 16.
12. Wander, W.E. Jr. Water Pollution Control Federation Highlights, 10 D-1, March 1973.
13. Tarazi, D.S. et al. Comparison of Wastewater Sampling Techniques J.W.P.C.F. 42 pp. 708-732 May 1970.
14. Associated Water and Air Resource Engineers, Inc. Handbook for Industrial Wastewater Monitoring. U.S. Environmental Protection Agency, Technology Transfer, August 1973.

CHAPTER 3

FLOW MEASUREMENTS

Methods of flow measurements are presented in this section. More detailed information can be found in a number of noteworthy publications such as ASME Monograph of Fluid Meters, (1) USDI Bureau of Reclamation's Water Measurement Manual, (2) publications of Techniques of Water Resource Investigations. by USDI, U.S. Geological Survey, as well as texts or manuals on hydraulics. (3-13)

Inaccurate flow measurements will lead to inaccurate flow proportional composite samples which in turn will lead to inaccurate results. Therefore, care must be exercised in selecting a flow measurement site. The ideal site gives desired flow measurement to meet program objectives, provides ease of operation and accessibility; personnel and equipment safety, and freedom from vandalism.

A flow measurement system usually consists of a primary device having some type of interaction with the fluid and a secondary device which translates this interaction into a desired readout or recording.(5)

Flow measurement methods can be broadly grouped into four categories:

1. Closed conduit flow measurement
2. Flow measurement for pipes discharging to atmosphere
3. Open channel flow measurement
4. Miscellaneous methods of flow measurement

Table 3.1 lists different methods of flow measurement and their application to various types of problems.

3.1 CLOSED CONDUIT FLOW MEASUREMENT

Some of the most commonly used devices and methods for closed conduit primary flow measurement are described briefly in this section.

3.1.1 Venturi Meter

The Venturi meter is one of the most accurate primary devices for measuring flow rates in pipes. Basically the Venturi meter is a pipe segment consisting of an inlet section (a converging section), a throat and an outlet section (a diverging section) as illustrated in Figure 3.1. A

TABLE 3.1 METHODS OF FLOW MEASUREMENT AND THEIR APPLICATION
TO VARIOUS TYPES OF PROBLEMS (14)(15)

Device or Method	Flow Range Measurement	Applicable to Type of Water and Wastewater	Cost	Ease of Installation	Accuracy* of Data	Pressure Loss Thru the Device	Volumetric Flow Detector	Flow Rate Sensor	Transmitter Available	Application
Mathematical formula	Small to large	All	Low	NA	Fair	NA	NA	NA	NA	Open channel, pipe flow
Water meters	Small to large	All	Low	Fair	Excellent	Medium	NA	NA	NA	Pipe flow
Bucket & stopwatch	Small	All	Low	Fair	Good	NA	NA	NA	NA	Small pipes with ends or joints can be disconnected
Pump capacity & operation	Small to large	All	Low	Fair	Good	NA	NA	NA	NA	Lines where water is being pumped
Floating objects	Small to medium	All	Low	NA	Good	NA	NA	NA	NA	Open channels
Dyes	Small to medium	All	Low	NA	Fairly good	NA	NA	NA	NA	Pipe flow and open channels
Salt Dilution	Small to medium	All	Low	NA	Fair	NA	NA	NA	NA	Pipe flow and open channels
Orifice meter	Small to large	Clean water	Medium	Fair	Excellent 1/4 - 2%	High	Yes	Yes	Yes	Pipe flow
Venturi tubes	Small to large	Clean water, limited for waters with suspended solids	High	Fair	Excellent 1/4 - 3%	Minimal	Yes	Yes	Yes	Pipe flow

* Assumes proper installation and maintenance of primary device

(continued)

TABLE 3.1 (Continued)

Device or Method	Flow Range Measurement	Applicable to Type of Water and Wastewater	Cost	Ease of Installation	Accuracy* of Data	Pressure Loss Thru the Device	Volumetric Flow Detector	Flow Rate Sensor	Transmitter Available	Application
Flow nozzle	Small to large	Clean water	Medium	Fair	Excellent 1/4 - 3%	Minimal	Yes	Yes	Yes	Pipe flow
Pitot tubes	Small to medium	Clean water	Medium	Fair	Good 2 - 5%	Minimal	Yes	Yes	Yes	Pipe flow
Elbow taps	Small to medium	Clean water, limited for water with suspended solids	Medium	Fair	Fair	None	Yes	Yes	Yes	Pipe flow
Rotameters	Small to medium	Clean water, limited for water with suspended solids	Medium	Fair	Excellent	Average	Yes	Yes	Yes	Pipe flow
Magnetic flow-meters	Small to large	All	High	Fair	Excellent 1/2 - 1%	None	Yes	Yes	Yes	Pipe flow
Weirs	Small to large	All	Medium	Difficult	Good to Excellent 2 - 5%	Minimal	Yes	Yes	Yes	Open channel flow
Flumes	Small to large	All	High	Difficult	Good to Excellent 2 - 5%	Minimal	Yes	Yes	Yes	Open channel flow
Acoustic flow-meters	Small to large	All	High	Fair	Excellent 1%	None	Yes	Yes	Yes	Pipe and open channel flow

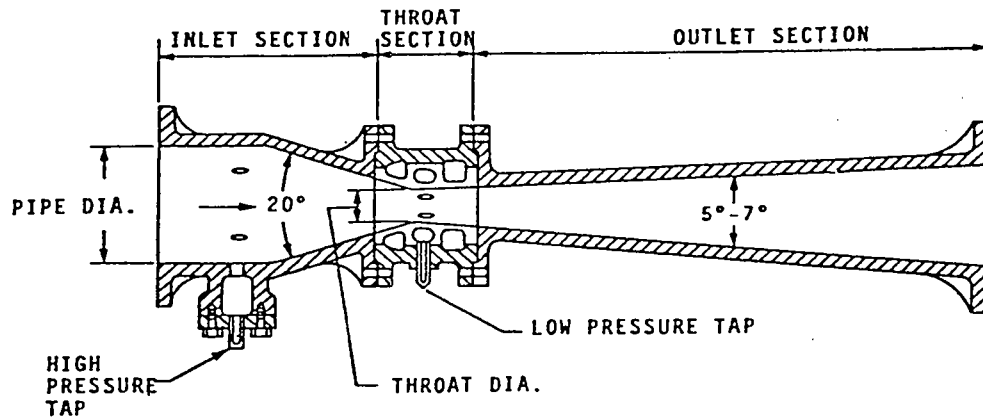


Figure 3.1 Venturi Meter (5)

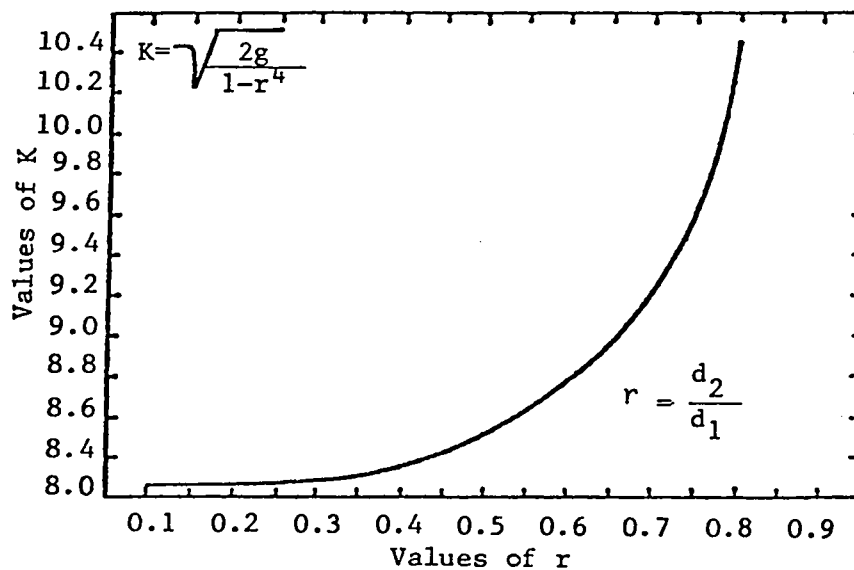


Figure 3.2 Curve for Determining the Values of K used in the Orifice, Venturi, and Flow Nozzle Equations (3)

portion of potential energy transferred to kinetic energy in the throat section causes a pressure differential which is proportional to the flow rate. One of the advantages of the Venturi meter is that it has low pressure loss.

Manufacturers of Venturi meters routinely size their meters for a specific use. The accuracy of the Venturi meter is affected by changes in density, temperature, pressure, viscosity and pulsating flow of the fluid.

To obtain accurate flow measurements:

1. Install Venturi meter as per manufacturer's instructions.
2. Install Venturi meter downstream from a straight and uniform section of pipe, at least 5-20 diameters, depending upon the ratio of pipe diameter to throat diameter and whether straightening vanes are installed upstream. Installation of straightening vanes upstream will reduce the upstream piping.
3. For wastewater application, insure that the pressure measuring taps are not plugged.
4. Calibrate Venturi meter in place either by volumetric method (Section 3.4.5) or comparative salt dilution method (Section 3.3.1.3) to either check the manufacturer's calibration curve or to develop a new calibration curve.(16)

The formula for calculating the flow in a Venturi meter is as follows:

$$Q = CAK \sqrt{H}$$

Where:

Q = volume of water, in cubic meters per second (cubic feet per second)
 C = discharge coefficient, approximately 0.98. C varies with Reynold's number, meter surfaces and installation.

A = Throat area, in square meters (feet) $\frac{\pi}{4} d_2^2$

H = $H_1 - H_2$, differential head, in meters (feet) of water.

H_1 = pressure head at center of pipe at inlet section, in meters (feet) of water.

H_2 = pressure head at throat, in meters (feet) of water

$$K = \sqrt{\frac{2g}{1 - \left(\frac{d_2}{d_1}\right)^4}} \quad (\text{Obtain values of K from Figure 3.2})$$

Where:

g = acceleration due to gravity, 9.82 m per sec² (32.2 feet per sec²)

- d_2 = throat diameter, in meters (feet).
- d_1 = diameter of inlet pipe, in meters (feet).

3.1.2 Flow Tubes

Included in the class of flow tubes are Dall tube, "Lo-Loss" tube, and gentle tube.

The Dall tube is a Venturi type device, in which the differential pressure results from the streamlined bending as well as the velocity head (Figure 3.3).

The Dall tube is almost as accurate and has a higher head recovery than the standard Venturi, being one of the lowest permanent head loss devices known. It is more sensitive to system disturbances than the Venturi, and straight upstream pipe runs of 40 pipe diameters or more may be required. Installation of straightening vanes upstream will reduce the upstream piping requirement. Although somewhat cheaper than the Venturi, the Dall tube must still be considered expensive. It is much shorter than either long or short tube Venturi meters. Calibration and other installation guidelines for Venturi meters also apply to flow tubes.

3.1.3 Flow Nozzle

A flow nozzle is a measuring device with characteristics between the Venturi meter and an orifice as far as head loss and cost are concerned (Figure 3.4). It operates on the same principles as the Venturi meter. The flow formula for the Venturi tube is also applicable to the nozzle. Flow nozzles can be used in wastewater flows containing moderate amounts of suspended solids. Each manufacturer uses a slightly different nozzle ranging from a Venturi to an orifice. Accuracy, installation and calibration guidelines for Venturi meters also apply to flow nozzles.

3.1.4 Orifice Meter

An orifice meter is relatively inexpensive, easy to install, and a reliable flow measuring device. Basically, an orifice is an obstacle placed in the path of flow in a pipe.

The principles of operation of an orifice are the same as for nozzles and Venturi meters since the stream lines of the flow and the basic formula are similar to those of a Venturi meter.

$$Q = CAK\sqrt{H} \quad (\text{Same as Venturi tube})$$

The coefficient, C, is illustrated for several forms of orifices in Figure 3.5 and tabulated in Table 3.2. The nominal coefficients are applicable for relatively large orifices operating under comparatively large heads of water.

The orifice measures flow over a wide range by varying the throat width. Orifice plates are the most sensitive of all the differential pressure

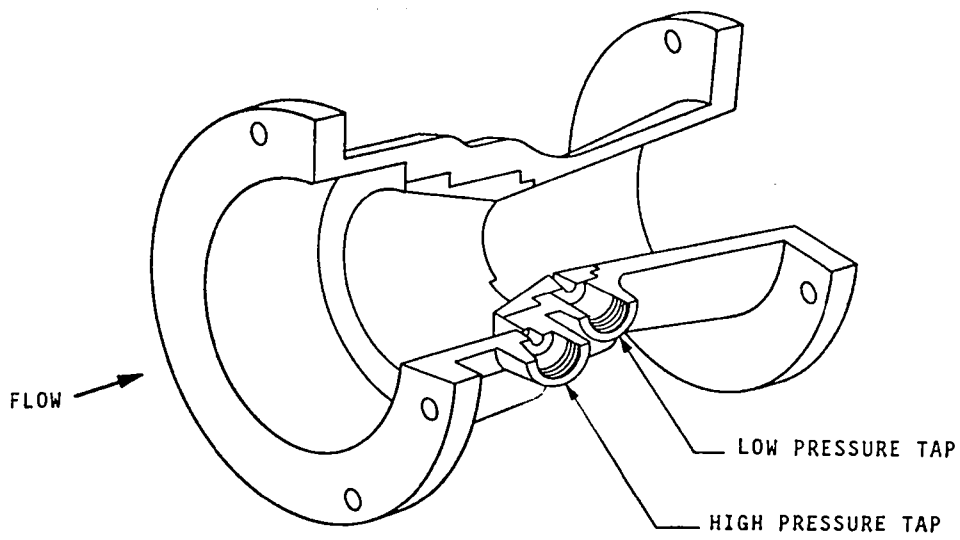


Figure 3.3 Dall Flow Tube (5)

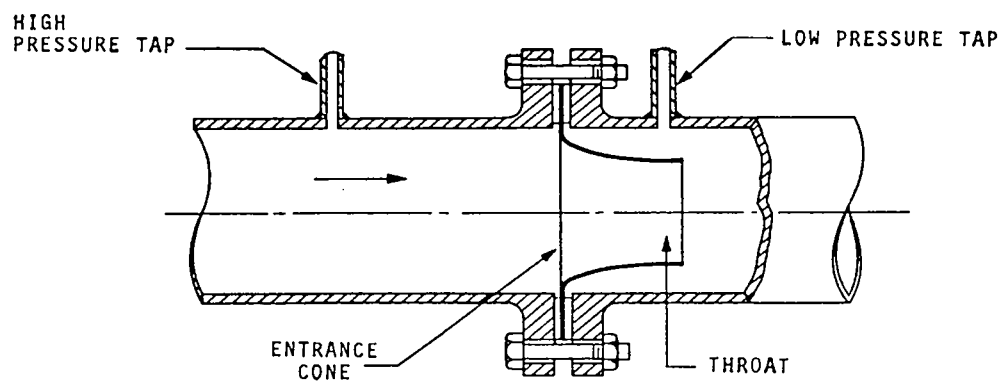


Figure 3.4 Typical Flow Nozzle Installation (5)

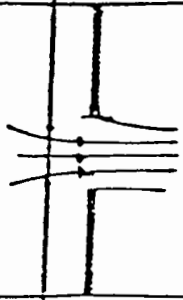
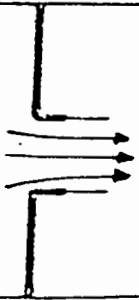
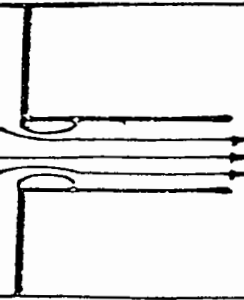

ORIFICES AND THEIR NOMINAL COEFFICIENTS				
	SHARP EDGED	ROUNDED	SHORT TUBE	BORDA
				
C	0.61 to 0.71	0.98	0.80	0.51

Figure 3.5 Coefficients of Several Types of Orifices (13)

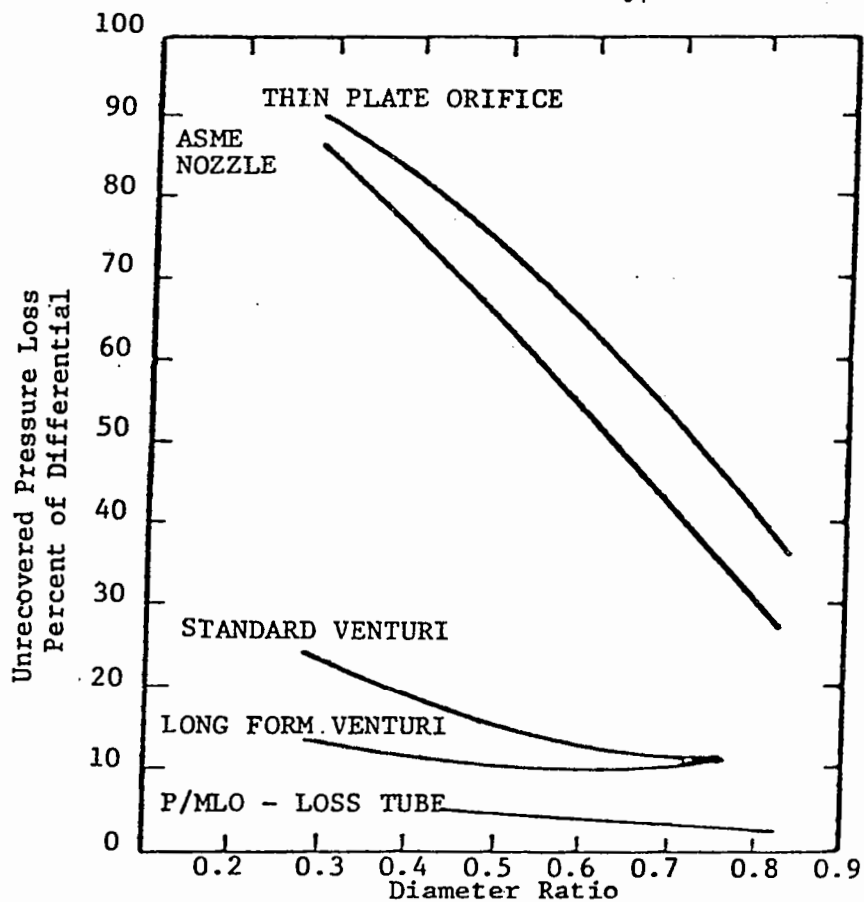


Figure 3.6 Relative Permanent Loss of Primary Elements (3)

TABLE 3.2 DISCHARGE COEFFICIENTS FOR PRESSURE TAP, ORIFICES (13)

Orifice Diameter Pipe Diameter	$\frac{d_2}{d_1}$	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Coefficient C		---	0.61	0.61	0.61	0.61	0.61	0.64	0.71

devices to effects of upstream disturbances. It is not uncommon to need 40 to 60 pipe diameters of straight run upstream of the installation.(3) The main disadvantage to the orifice is the large permanent pressure loss that occurs across the section. The other disadvantage of the orifice is susceptibility to clogging in waters with high suspended solids concentration. The relative permanent pressure losses for the Venturi tube, the nozzle, P/M Lo-Loss tube (Badger Meter Inc.) and the orifice are compared in Figure 3.6.

3.1.5 Elbow Meters

Flow acceleration induced in a fluid going around a bend such as an elbow produces a differential pressure that can be used to indicate flow. The pressure on the outside of an elbow is greater than on the inside, and the pressure taps located midway around the bend at about 45 degrees from either flange can be connected to a suitable secondary element for indicating or recording.

For accurate flow measurement, straight pipe runs of at least 20 pipe diameters should be provided both upstream and downstream of the elbow. accuracies of 3 to 10% are generally encountered although accuracies of 1 to 2% or better in some cases may be achieved if calibrated in place.(5)

3.1.6 Pitot Tube

A schematic diagram of a simple Pitot tube is shown in Figure 3.7. In operation, the velocity of the flow is calculated from the difference in head measured on the manometer. Pitot tubes measure the flow velocity at a point.

The basic formula is:

$$V_x = C \sqrt{2gH}$$

$$V_x = \text{velocity at a point (at center of pipe } V_x = V_c)$$

C = coefficient of discharge obtained by calibration

$$V_c = \text{velocity at the center}$$

$$V_m = \text{mean velocity} \approx 0.83 V_c$$

$$H = \text{measured pressure differential (} P_2 - P_1 \text{ in Figure 3.7)}$$

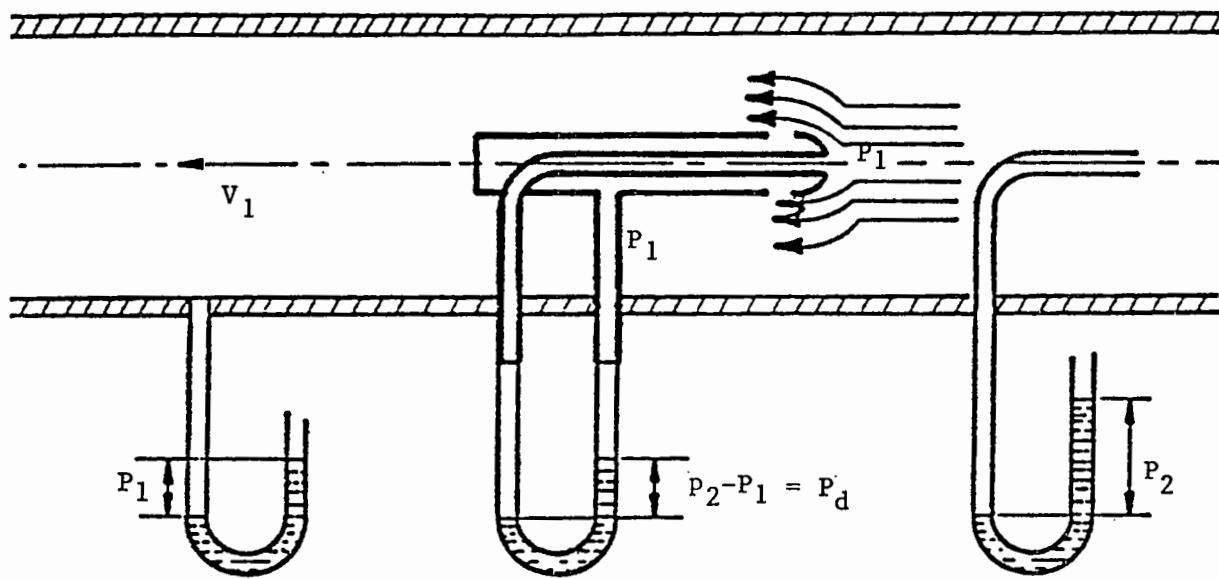


Figure 3.7 Pitot Tube Schematic

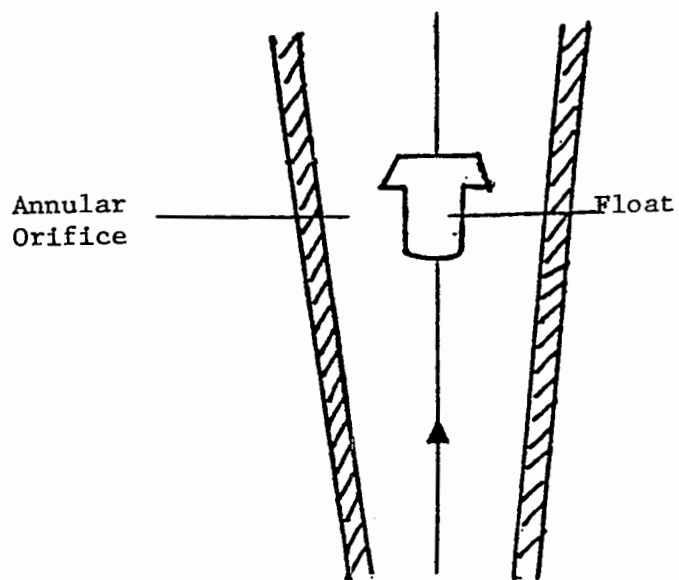


Figure 3.8 Rotameter

Q = discharge volume

A = area of cross section of stream at the point of measurement

$$Q = V_m A$$

Commercially available Pitot tubes consist of a combined peizometer and total head meter. Pitot tube measurements should be made in a straight section upstream and free of valves, tees, elbows, and other fittings with a minimum distance of 15 to 50 times the pipe diameter. When a straight section is not possible, a velocity profile should be obtained experimentally to determine the point of mean velocity. Pitot tubes are not practical for use with liquids with large amounts of suspended solids because of the possibility of plugging. In large pipes, the Pitot tube is one of the most economical means of measuring flows, except for low velocities.

3.1.7 Rotameters

Rotameters (Figure 3.8) are tapered tubes in which the fluid flows vertically upward. A metal float in the tube comes to equilibrium at a point where the annular flow area is such that the velocity increase has produced the necessary pressure difference. Rotameters are simple, inexpensive and accurate devices for measuring relatively small rates of flow of clear, clean liquids (no suspended solids). For this reason they are used to measure the water rate into individual processing steps in manufacturing operations. To maintain accuracy in a rotameter, it is essential that both the tube and float be kept clean.

3.1.8 Electromagnetic Flowmeter

The electromagnetic flowmeter operates according to Faraday's Law of Induction: the voltage induced by a conductor moving at right angles through a magnetic field will be proportional to the velocity of the conductor through the field. In the electromagnetic flowmeter, the conductor is the liquid stream to be measured and the field is produced by a set of electromagnetic coils. A typical electromagnetic flowmeter is shown in Figure 3.9. The induced voltage is subsequently transmitted to a converter for signal conditioning.

Electromagnetic flowmeters are used in full pipes and have many advantages: accuracies of ± 1 percent, a wide flow measurement range, a negligible pressure loss, no moving parts, and rapid response time. However, they are expensive and build-up of grease deposits or pitting by abrasive wastewaters can cause error. Regular checking and cleaning of the electrodes are necessary.

3.1.9 Acoustic Flowmeters

Acoustic flowmeters, commonly used in water and wastewater flow measurements, operate on the basis of travel time difference method. In the travel time difference method, sound waves are transmitted diagonally across

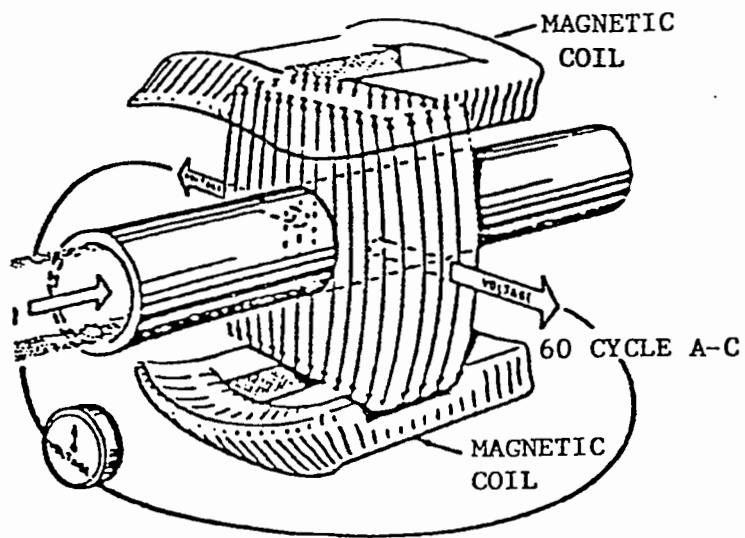


Figure 3.9 Electromagnetic Flowmeter

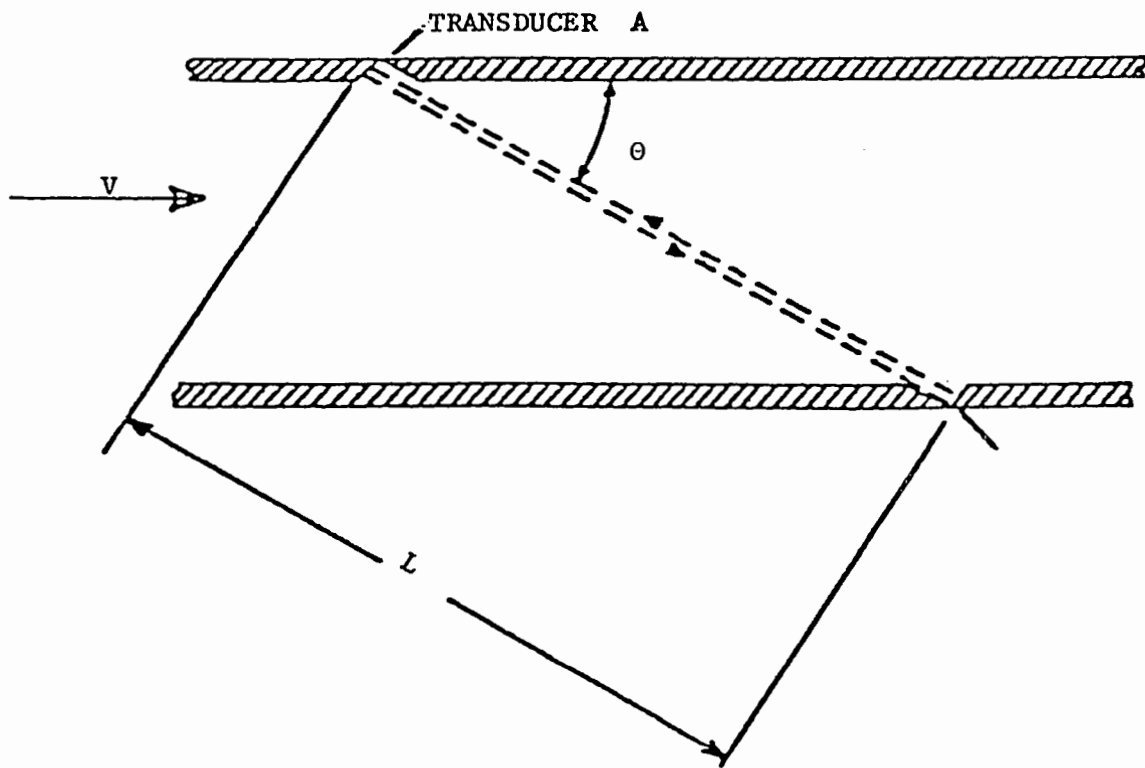


Figure 3.10 Principle of Acoustic Flowmeter (6)

the pipe or channel in opposite directions relative to the flow and the difference in travel times upstream and downstream are measured (Figure 3.10).

Flowmeters must be installed according to manufacturer's instructions and calibrated in place to eliminate errors due to uncertainties in non-laminar flow profile, and due to acoustic short circuit (where transducers are mounted externally on the pipe). According to the manufacturers, an accuracy of one percent of full scale is achievable.
(2)(5)

3.2 FLOW FROM PIPES DISCHARGING TO THE ATMOSPHERE

The common techniques for measuring the flow from open ended pipes either full or partly full are listed below. The orifice and flow nozzle techniques which are not listed here are described in Sections 3.1.3 and 3.1.4 respectively. Rotating element meters are described in Section 3.3.1.1.

3.2.1 Pipes Flowing Full

1. Vertical open end pipe (7)

a. Weir flow: $Q = 0.249D^{1.20}H^{1.24}$ (Figure 3.11a)

b. Jet flow: $Q = 0.171D^{2.025}H^{0.53}$ (Figure 3.11b)

where: Q = flow, m^3/s

D = internal pipe diameter, meters

H = distance from pipe outlet to top of crest,
meters

2. Horizontal or sloped open end

$$Q = 2.264 \times 10^{-4} \frac{AX}{\sqrt{Y}} \quad (\text{Figure 3.11c and e})$$

where: Q = flow, m^3/s

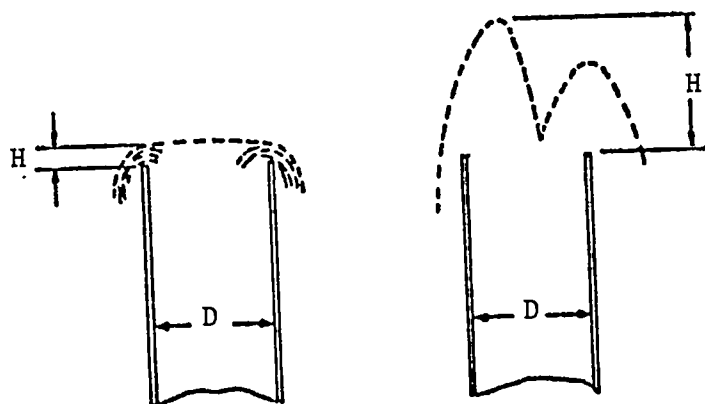
A = cross sectional area of the pipe, square meters

X = distance from the end of the pipe to where Y is
measured, meters

Y = vertical distance measured at a distance X from
the pipe end, meters

3. Purdue Method (6)

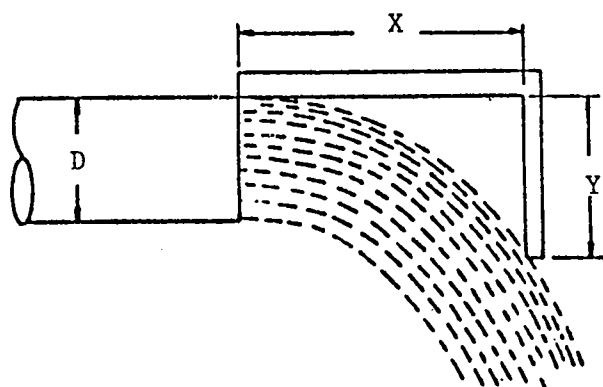
It is similar to the trajectory method for the horizontal open ended



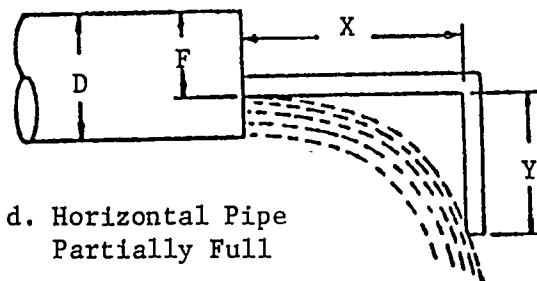
a. Weir Flow

b. Jet Flow

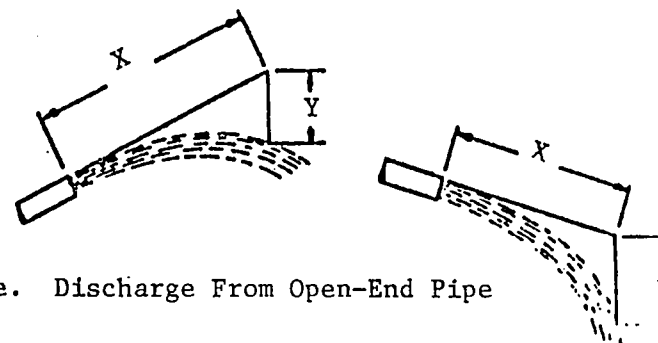
Vertical Open-End Pipe



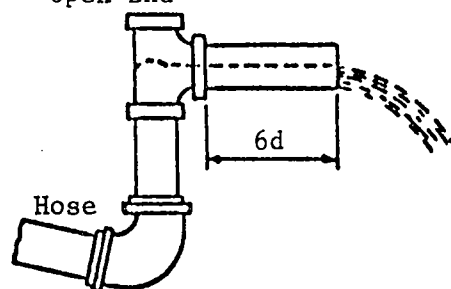
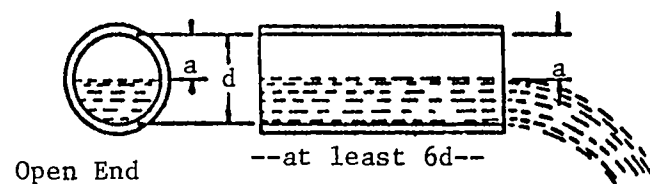
c. Horizontal Pipe Flowing Full



d. Horizontal Pipe Partially Full



e. Discharge From Open-End Pipe



f. California Pipe Method

Figure 3.11 Techniques for Pipes Discharging to the Atmosphere (7)

pipe, described in (2) above. To obtain the flow, the trajectory measurements X and Y, Figure 3.12, are used with curves derived from Purdue University experiments on pipes 0.05 to 0.15 m (2 to 6 inches) in diameter. Figure 3.13 gives discharge data for Purdue trajectory method for X = 0, 6, 12, and 18 inches and inside pipe diameters of two, four and six inches.

3.2.2 Pipes Flowing Partially Full

1. Horizontal or sloped open end (7)

$$Q = \frac{2.264 \times 10^{-4} AX(CF)}{\sqrt{Y}} \quad (\text{Figure 3.11d})$$

where:

Q = flow, m³/s

A = cross sectional area of the pipe, square meters

X = distance from end of pipe to where Y is measured, meters

Y = vertical distance measured at a distance X from the pipe end, meters

CF = correction factors which are given in Table 3.3

2. Purdue Method (6)

This method can be used for partially full pipe discharging to atmosphere using the curves (Figure 3.12) for X = 0, provided the brink depth is less than 0.8 diameter.

3. California Pipe Method (6)(7)

$$Q = TW, (\text{Figure 3.11f})$$

where:

Q = flow, m³/s

T = 8.69 (1 - $\frac{a}{d}$)^{1.88}

W = d^{2.48}

d = Inside pipe diameter, meters

a = Inside distance from the top of pipe to water surface, meters

The empirical equation is derived from experiments performed on steel pipes from 3 to 10 inches in diameter and it is imperative that a/d should be less than 0.5 and the straight pipe length to the end of pipe should be at least 6d.

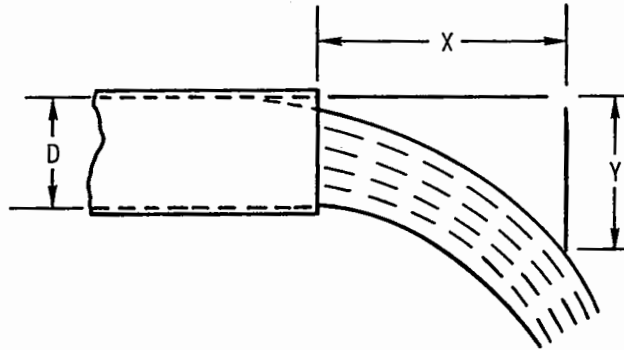


Figure 3.12 Trajectory Measurements, Purdue Method

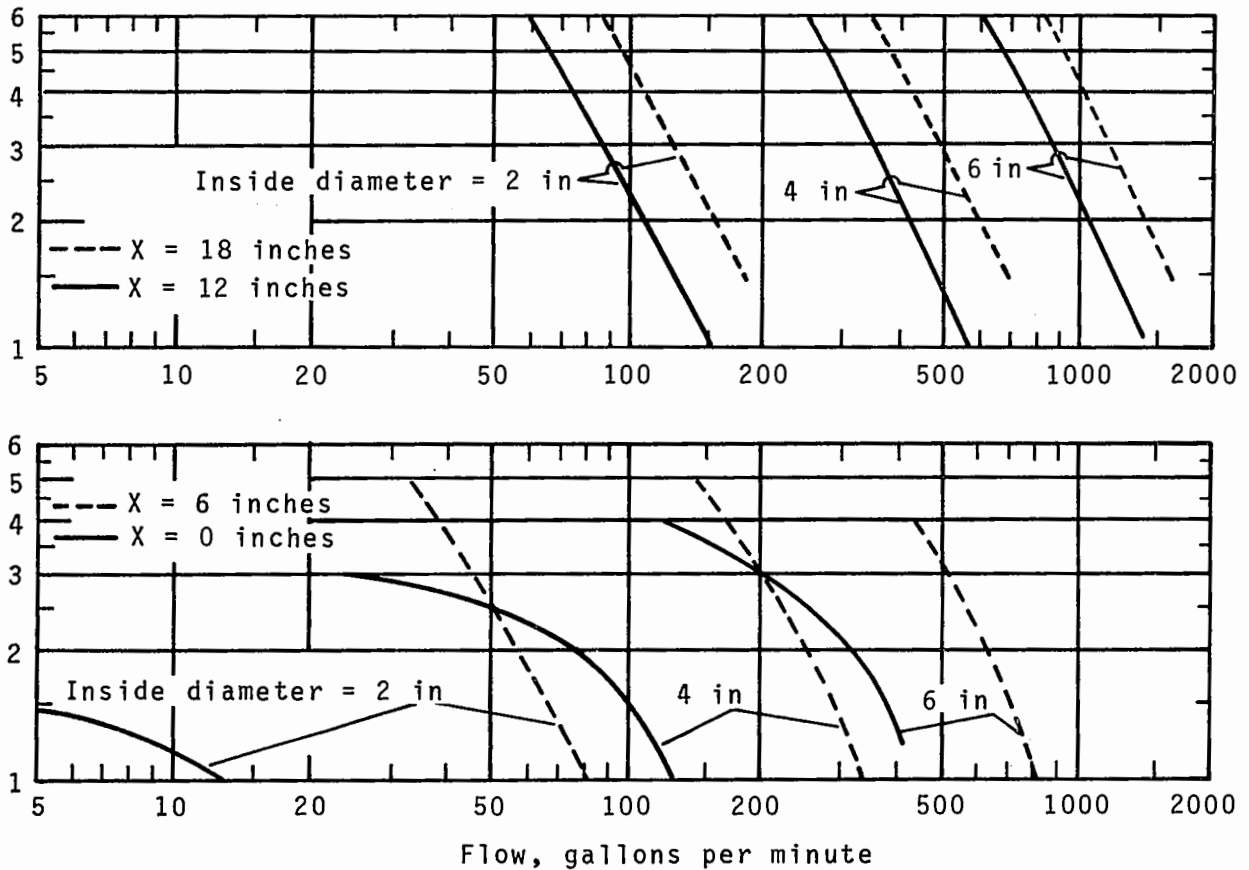


Figure 3.13 Discharge Data, Purdue Method

TABLE 3.3 CORRECTION FACTORS FOR DISCHARGE FROM PIPES
PARTLY FULL (7), HORIZONTAL OR SLOPED END

R*	Correction Factor	R*	Correction Factor	R*	Correction Factor
0.10	0.948	0.37	0.664	0.64	0.324
0.11	0.939	0.38	0.651	0.65	0.312
0.12	0.931	0.39	0.639	0.66	0.300
0.13	0.922	0.40	0.627	0.67	0.288
0.14	0.914	0.41	0.614	0.68	0.276
0.15	0.905	0.42	0.602	0.69	0.265
0.16	0.896	0.43	0.589	0.70	0.253
0.17	0.886	0.44	0.577	0.71	0.241
0.18	0.877	0.45	0.564	0.72	0.230
0.19	0.867	0.46	0.551	0.73	0.218
0.20	0.858	0.47	0.538	0.74	0.207
0.21	0.847	0.48	0.526	0.75	0.195
0.22	0.837	0.49	0.513	0.76	0.184
0.23	0.826	0.50	0.500	0.77	0.174
0.24	0.816	0.51	0.487	0.78	0.163
0.25	0.805	0.52	0.474	0.79	0.153
0.26	0.793	0.53	0.464	0.80	0.142
0.27	0.782	0.54	0.449	0.81	0.133
0.28	0.770	0.55	0.436	0.82	0.123
0.29	0.759	0.56	0.423	0.83	0.114
0.30	0.747	0.57	0.411	0.84	0.104
0.31	0.735	0.58	0.398	0.85	0.095
0.32	0.723	0.59	0.386	0.86	0.086
0.33	0.712	0.60	0.373	0.87	0.078
0.34	0.700	0.61	0.361	0.88	0.069
0.35	0.688	0.62	0.349	0.89	0.061
0.36	0.676	0.63	0.336	0.90	0.052

* R = F/D (Free board in pipe/inside pipe diameter), (see Figure 3.11d)

3.3 OPEN CHANNEL FLOW MEASUREMENTS

Methods of flow measurements for open channels can be applied to flows in non-pressure sewers since both have the same hydraulic characteristics. Different methods in use can be grouped into the following broad classification:

1. Velocity Methods
2. Head-Discharge Methods
3. Miscellaneous Techniques

3.3.1 Velocity Methods

Velocity flow can be measured using drag body current meters, eddy-shedding current meter, acoustic velocity meter, doppler-shift velocity meter, electromagnetic current meter, and rotating element current meters. Various drag body current meters are compared in Table 3.4 and Pitot tubes in Section 3.1.6.

3.3.1.1 Rotating Element Current Meters

Of the rotating element current meters, Price and Pigmy meters are commonly used. The principle of operation is based on the proportionality between the velocity of water and resulting angular velocity of the meter rotor. In conventional current meters there is a wheel which rotates when immersed in flowing water and a device which determines the number of revolutions of the wheel. The general relation between the velocity of the water and number of revolutions of the wheel is given by:
(1)(2)(4)(5)(6)(17):

$$V = a + bN,$$

where:

V = velocity of water meters per second
a and b are constants
N = number of revolutions per second

These current meters can be grouped into two broad classes:
1) vertical-axis rotor with cups or vanes and 2) horizontal-axis with vanes. Figure 3.14 shows the propeller current meter which is typical of a horizontal-axis current meter with vanes. Figure 3.15 shows the Price current meter which is typical of a vertical-axis rotor current meter with cups.

Practical considerations limit the ratings of these meters to velocities of 0.030 m/s (0.11 fps) to about 4.57 m/s (15 fps). The comparative characteristics of these two types are summarized below: (4)

1. Vertical-axis rotor with cups or vanes
 - a. Operates in lower velocities than do horizontal-axis meters.
 - b. Bearings are well protected from silty water.
 - c. Rotor is repairable in the field without adversely affecting the rating.
 - d. Single rotor serves for the entire range of velocities.

TABLE 3.4 COMPARISON OF DRAGBODY CURRENT METERS (17)

Factor	Dragbody Current Meter Type				
	Vertical Axis Deflection Vane	Horizontal Axis Pendulum Type Deflection Vane	Pendulum Current Meter	Inclinometer	Drag Sphere
Velocity Range	Wide range but not suitable for low velocities	Wide range	Wide range	Suitable for low velocities-only single velocity range	Single velocity range
Submerged Installation	No	Possible	Pendulum ball is submerged	Possible	Possible
69 Debris	Problem	Not a Problem	Affects drag on line and hence accuracy of velocity measurement	Not a problem	Not a problem
Output Recording	Mechanical output	Electrical output	No, manual operation	No, data manually processed	Electrical output
Readout of Deflection	Visual	No visual readout	-	-	Deflection can be resolved-no visual readout
Simplicity	Simple	Simple	Complex		

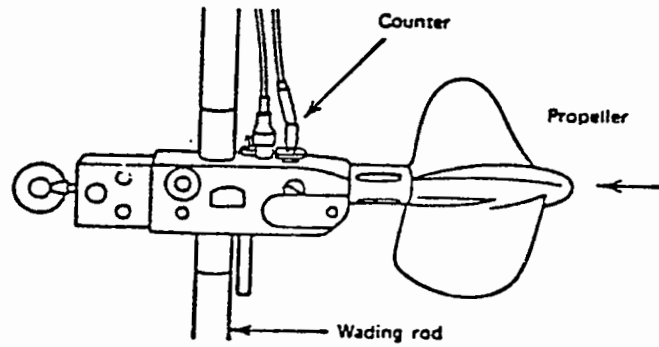


Figure 3.14 Propeller Meter (16)

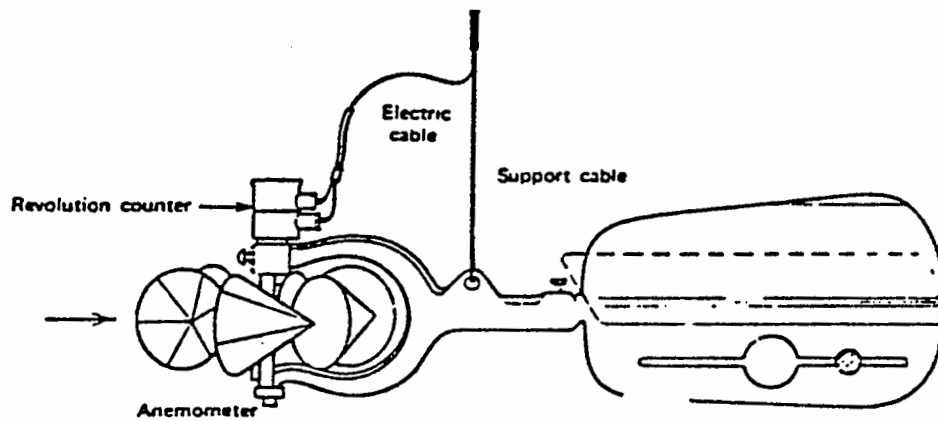


Figure 3.15 Price Meter (16)

2. Horizontal-axis rotor with vanes

- a. Rotor disturbs flow less than do vertical-axis rotors because of axial symmetry with flow direction.
- b. Rotor is less likely to be entangled by debris than are vertical-axis rotors.
- c. Bearings friction is less than for vertical-axis rotors because bending moments on the rotor are eliminated.
- d. Vertical currents will not be indicated as positive velocities as they are with vertical-axis meters.
- e. They have a higher frequency of mechanical problems.

To determine the discharge (flow volume), in additions to velocity of flow it is necessary to determine the area of flowing water or wastewaters. This holds especially for large flows in rivers, lakes, and wide and deep channels. A depth sounding is necessary at each vertical and width measurement of the cross-section of flow to determine the area of flowing water or wastewater. Sounding rods, sound weights and reels, handlines, and sonic sounders are common equipment used for depth determinations. Marked cableways and bridges, steel or metallic taps or tag lines are used for width determinations. For details or procedures for depth and width determinations, see reference.(4)

3.3.1.2 Measurement of Velocity

To determine the discharge at a particular cross-section, it is necessary to determine the mean velocity of flow at that section. In drag body current meters such as vertical-axis deflection vane, horizontal-axis pendulum type deflection vane and pendulum current meters, it is possible to integrate velocities at different depths in a particular section to obtain the mean velocity of flow, whereas inclinometer, drag sphere, rotating element current meters and pitot tubes measure velocity at a point. Therefore, to obtain the mean velocity of flow at a particular vertical section, it is necessary to take velocity measurements at different depths. The various methods of obtaining mean velocities are:

1. Vertical-velocity curve
2. Two-point
3. six-tenths depth
4. Two-tenths depth
5. Three point
6. Subsurface

Table 3.5 compares these methods in relation to application, flow depth, velocity measuring point(s), and accuracy.

3.3.1.3 Time of Travel-Velocity Methods

1. Salt Velocity Method (1)(2)(5)(6)

The method is based on the principle that salt in solution increases the conductivity of water. This method is suitable for open channels of

TABLE 3.5 COMPARISON OF VARIOUS METHODS TO OBTAIN MEAN VELOCITY

Methods Considerations	Vertical-Velocity Curve Method	Two-point Method	Six-tenth depth Method	Two-tenth Depth Method	Three point Method	Subsurface Method
Application	Not for routine discharge and measurements To determine coefficients for application to the results obtained by other methods	Generally used	Primarily used for depths less than 2.5 feet	During times of high velocities when measurements at 0.6 and 0.8 depth are not possible	When velocities in a vertical are abnormally distributed When more weight to 0.2 and 0.8 depth observations is desired	When it is impossible to obtain soundings and the depth cannot be es- timated to an approximate 0.2 depth setting
Flow depth requirement	Greater than 2.5 feet	Greater than 2.5 feet	0.3 foot to 2.5 feet	No depth constraint	Greater than 2.5 feet	Greater than 2.5 feet
Velocity measuring point(s)	At 0.1 depth increments be- tween 0.1 and 0.9 depth	0.2 and 0.8 depth below the water surface	0.6 depth below the water surface	0.2 depth below the water surface	0.2, 0.6 and 0.8 depth below the water sur- face	At least 2 feet below the water surface
Mean velocity	From vertical- velocity curve	$\frac{V_{0.2} + V_{0.8}}{2}$	Observed velocity is the mean velocity	$V_{mean} = C \times V_{0.2}$ C=Coefficient obtained from vertical-velocity curve. At that vertical for the particular depth of flow	$V_{mean} = \frac{V_{0.2} + V_{0.8} + V_{0.6}}{4}$	$V_{mean} = C \times V_{observed}$ C=Coefficient obtained from vertical-velo- city curve at that vertical for the parti- cular depth of flow
Accuracy	Most Accurate	Gives consistent and accurate re- sults	Gives reliable results	If C is accu- rately known can give fairly reli- able results	Gives reliable results	Gives rough estimate as C is difficult to determine accurately

$V_{0.2}$ = Velocity at 0.2 depth from water surface

$V_{0.8}$ = Velocity at 0.8 depth from water surface

$V_{0.6}$ = Velocity at 0.6 depth from water surface

V_{mean} = Mean velocity

constant cross-section and for flow in pipes. Sodium chloride and lithium chloride are commonly used. The basic procedure is as follows:

- a. Install two pairs of conductivity electrodes down stream from the salt injection point at known distances and sufficiently far apart in the stretch of the channel.
- b. Connect the recording galvanometer to the electrodes.
- c. Inject the slug of salt solution.
- d. The time for salt solution to pass from the upstream to the downstream electrodes, in seconds, is determined by the distance on the graph between the centers of the gravity of the peak areas.
- e. Calculate the discharge, using the formula:

$$Q = \frac{AL}{T}, \text{ where,}$$

Q = discharge in cubic meters per second

A = cross-sectional area of flow, square meters

L = distance between the electrodes, meters

T = recorder time for salt solution to travel the distance between the electrodes, seconds.

2. Color Velocity Method

The color velocity method is used to estimate high velocity flows in open channels. It consists of determining the velocity of a slug of dye between two stations in the channel. This velocity, taken as the mean velocity, multiplied by the cross-sectional area of flow gives an estimate of the discharge. Commercially stable dyes (see section 3.4.3) or potassium permanganate may be used as the coloring matter. The color velocity is computed from the observations of the time of travel of the center of the mass of colored liquid from the instant the slug of dye is poured at the upstream station to the instant it passes the downstream station, which is at a known distance from the upstream station.

With fluorescent dyes, the use of a fluorometer to detect the center of the colored mass will enhance the accuracy of the results.

3. Floats

There are three types of float methods used for estimating flow measurements; surface floats, subsurface floats and integrating floats. To determine the flow velocity, one or more floats are placed in the stream and their time to travel a measured distance is determined. These methods are simple, but from an accuracy standpoint, they should only be used for estimating the discharge.

Various surface floats such as corks and stoppered bottles and submerged floats like oranges, measure the surface velocity. The mean velocity of flow is obtained by multiplying with a coefficient which varies from 0.66 to 0.80.(2)

A more sophisticated version is the rod-floats, which are usually round or square wooden rods. These rods have a weighted end so that they float in vertical position with the immersed length extending about nine-tenth of the flow depth. Velocity measured by the time of travel by these rods is taken as the mean velocity of flow. These floats are used in open channels and sewers.

To obtain better results, the velocity measurements should be made on a calm day when in a sufficiently long and straight stretch of channel or sewer of uniform cross-section and grade with a minimum of surface waves. Choose a float which will submerge at least one-fourth the flow depth.

A more accurate velocity measurement is obtained by using integrating float measurements. The method is simple and consists of the release of buoyant spheres resembling like ping pong balls from the channel floor. As these spheres rise, they are carried downstream by the flow velocity. The time from the moment of release to the moment when they surface, and the distance traveled downstream are measured and inserted into the following equations to determine the flow rate.

$$Q = DV \quad \text{and} \quad V = \frac{L}{t}$$

where: Q = discharge per unit width of channel in cubic meters/sec.
(cubic ft/sec.)
 D = flow depth, meters. (feet)
 V = terminal velocity of the float, meters/sec. (ft./sec.)
 L = distance traveled downstream by float, meters. (feet)
 t = time of rise of the float in seconds.

In flows of large depth and velocity, integrating float methods with two floats of different velocities of rise are used.(18)(19) The discharge is calculated using the relationship:

$$Q = \frac{D(L_2 - L_1)}{t_2 - t_1} \quad \text{where, } L_2 \text{ and } L_1 \text{ are distances traveled}$$

downstream by float 2 and float 1 respectively; and t_2 and t_1 are times of rise of float 2 and float 1 respectively.

The integrating float method is simple and does not require any laboratory calibration. It integrates the vertical velocity profile and yields the mean velocity or discharge per unit width of the section. The method is suited to low velocities and is especially useful for flows having abnormal velocity profiles, and it has practically no lower velocity limit. To get better accuracy, the reach of the stream to be measured should be sufficiently long and straight and the bed fairly uniform. Use a fast rising float so that distance travelled downstream is of short length. The shape of the float should be spherical. (18)

3.3.2 Head Discharge Methods

This technique takes advantage of the head discharge relationship that exists when a liquid flows over an obstruction or through a specific (convergent-straight-divergent) channel section.

3.3.2.1 Weirs

A weir is an overflow structure built across an open channel to measure the rate of flow of liquid.

Depending upon the shape of the opening, weirs may be termed rectangular, trapezoidal, or triangular. When the water level in the downstream channel is sufficiently below the crest to allow free access of air to the area beneath the nappe, the flow is said to be free. When the water level under the nappe rises above the crest elevation the flow may be considered submerged: the degree of submergence depends upon the ratio of upstream and downstream head (height of water above crest elevation). The effect of submergence is to cause large inaccuracies in the flow measurements. Therefore, the use of submerged weirs as the flow measuring device is avoided.

In a sharp crested weir, flowing liquid does not contact the bulk head but springs past it. If the bulk head is too thick for the liquid to spring past, the weir is classed as broad crested.

Weirs may be contracted or suppressed. When the distances from the sides of the weir notch to the sides of the channel (weir pool) are great enough (at least two or three times the head on the crest) to allow the liquid a free, unconstrained lateral approach to the crest, the liquid will flow uniformly and relatively slowly toward the weir sides. As the flow nears the notch it accelerates, and as it turns to pass through the opening, it springs free laterally with a contraction that results in a jet narrower than the weir opening. If a rectangular weir is placed in a channel whose sides also act as the sides of the weir, there is no lateral contraction, and the weir is called a suppressed weir. Various types of weirs are shown in Figure 3.16.

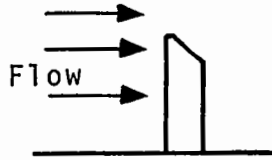
Most of the flow measurements are conducted on sharp crested weirs without submergence and the subsequent discussion is limited to this type. For information on sharp crested weirs with submergence and broad crested weirs, refer to reference 2 and other books on hydraulics.

A typical sharp crested weir is shown in Figure 3.17. Figures 3.18 a, b and c, show the various dimensions required for fully contracted rectangular Cipolletti and V-notch weirs.

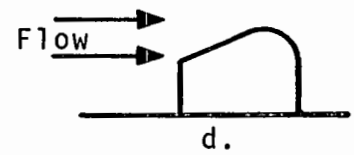
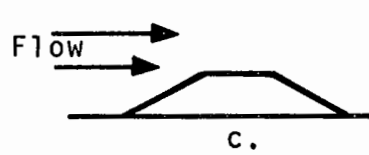
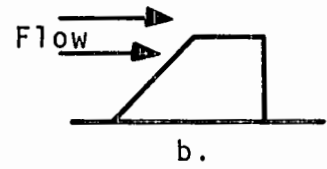
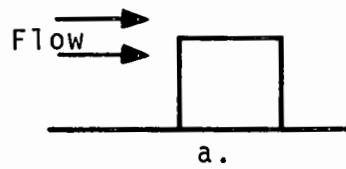
The relationship between head and discharge for different weirs is given in Table 3.6. For rectangular weirs, the Francis formula is widely used for flow measurements. However, it should be born in mind that it is applicable and accurate only for sharp crested fully contracted or suppressed weirs. On

SHAPE OF THE WEIR CREST

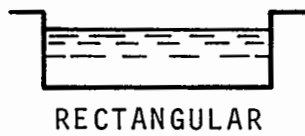
SHARP CRESTED



BROAD CRESTED WEIR



SHAPE OF THE NOTCH



RECTANGULAR



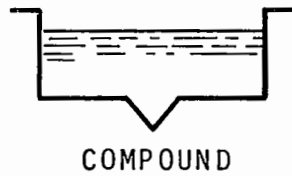
INVERTED
TRAPEZOIDAL



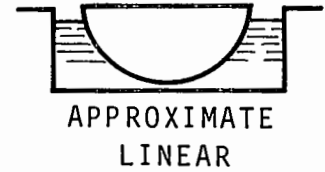
POEBING



V-NOTCH



COMPOUND



APPROXIMATE
LINEAR



TRAPEZOIDAL

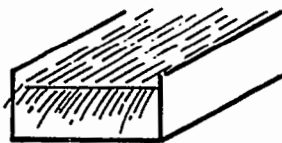


PROPORTIONAL

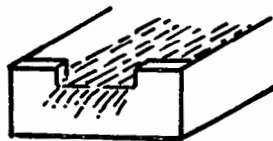


APPROXIMATE
EXPONENTIAL

FLOW CONTRACTION



SUPPRESSED



CONTRACTED

Figure 3.16 Types of Weirs

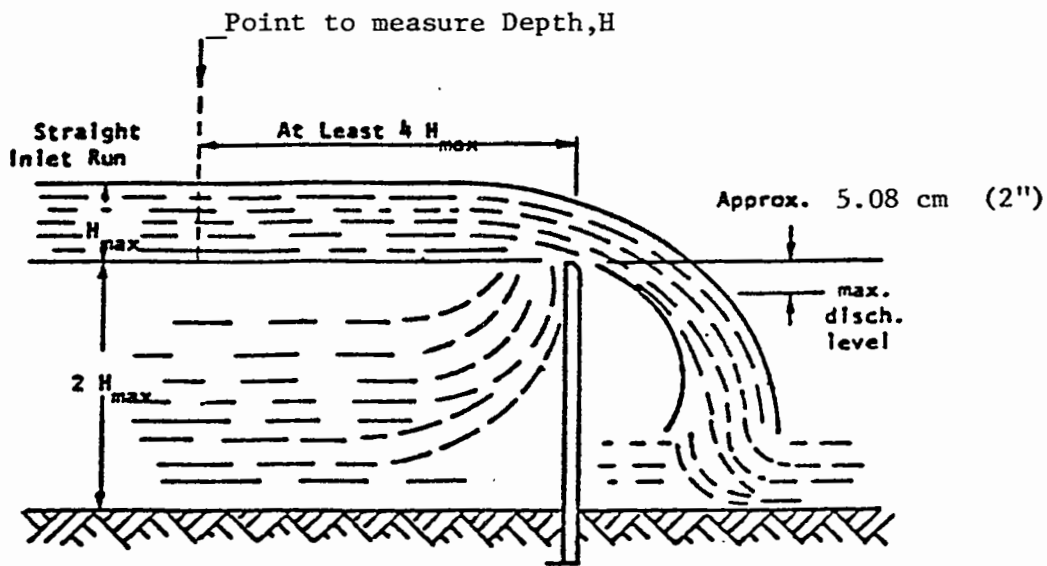
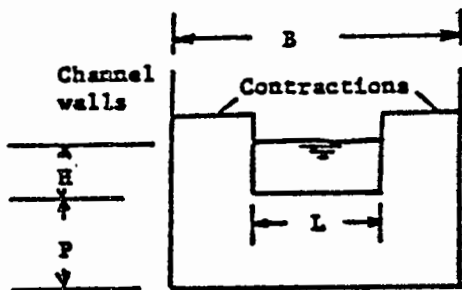
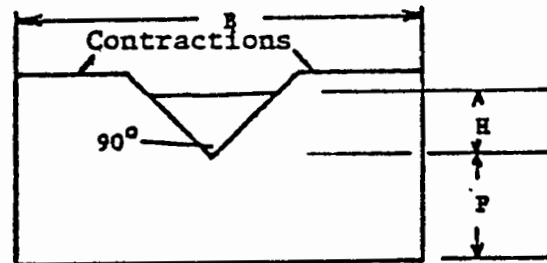


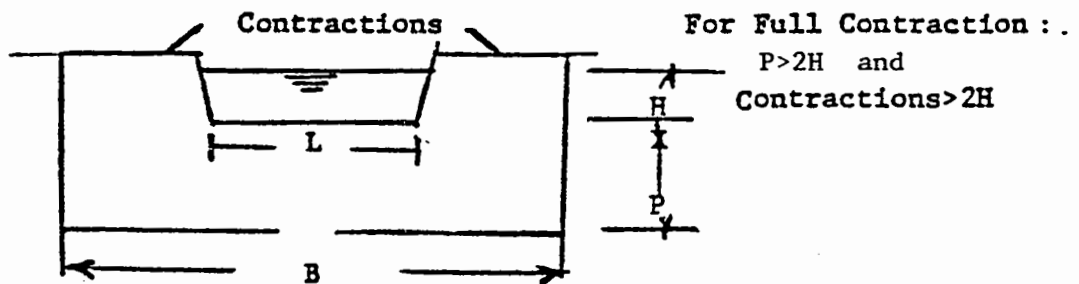
Figure 3.17 Typical Sharp Crested Weir (3)



a. Contracted Rectangular Weir



b. Contracted V - Notch Weir



c. Contracted Cipolletti Weir

Figure 3.18 Various Dimensions for Fully Contracted Rectangular, Cipolletti and V-Notch Weirs (6)

TABLE 3.6 HEAD-DISCHARGE RELATIONSHIP FORMULAS

Weir Type	Contracted	Suppressed	Remarks
<u>Rectangular</u>			
Francis Formulas	$Q = 3.33(L-0.2H)^{3/2}$	$Q = 3.33LH^{3/2}$	Approach velocity neglected
	$Q = 3.33\left\{(H+h)^{3/2} - h^{3/2}\right\} (L-0.2H)$	$Q = 3.33L\left\{(H+h)^{3/2} - h^{3/2}\right\}$	Approach velocity taken into consideration
Kindsvater-Carter formula	$Q = C_e L_e H_e^{1.5}$	$Q = C_e L_e H_e^{1.5}$	
<u>Cipolletti</u>	$Q = 3.367 LH^{3/2}$	NA	Approach velocity neglected
	$Q = 3.367L(H+1.5h)^{3/2}$	NA	Approach velocity taken into consideration
<u>V-Notch</u>			
Cone formula for 90° V-Notch only	$Q = 2.49 H^{2.48}$	NA	V-Notch weirs are not appreciably affected by approach velocity
Kindsvater-shen formula	$Q = \frac{8}{15} C_e \tan\left(\frac{\theta}{2}\right) (2gH_e^5)^{1/2}$	NA	

Q = discharge in cubic feet per second L = crest length in feet
 H = head in feet h = head in feet due to the approach velocity (V), $= 62/2g$
 C_e = coefficient, $L_e = L + k_b$, where k_b = ratio of crest (L) to channel width (B), $k_b = L/B$
 $H_e = H + 0.003$ NA = Not applicable
 θ = Angle of the notch $H_e = H + k_h$

the other hand the Kindsvater-Carter formula is applicable to any type of sharp crested rectangular weir. It gives accurate results and is being increasingly used.

The rate of flow determines the type of weir to use. A rectangular weir is preferable for flows greater than 3.4 cubic meters/min. (2 cubic feet/ sec.) V-notch weirs are used for flows of less than 0.17 cubic meters/min. (1.0 to 10 cubic feet/sec.).(2) The Cipolletti weir is also used in the same range as the rectangular weir. The accuracy of measurements obtained by the use of Cipolletti weirs, based on the formulas given in Table 3.6 is inherently not as great as that obtained with suppressed rectangular and V-notch weirs. (2)

With these ranges in mind, the minimum head should be at least 5 cm (0.2 ft.) to prevent nappe from clinging to the crest, and because at smaller depths it is difficult to get sufficiently accurate gauge readings. The crest should be placed high enough so that the water flowing over will fall freely, leaving an air space under and around the jets. Requirements for standard weir installations are shown in Figures 3.18 a,b, and c for rectangular, Cipolletti and V-notch weirs, respectively.

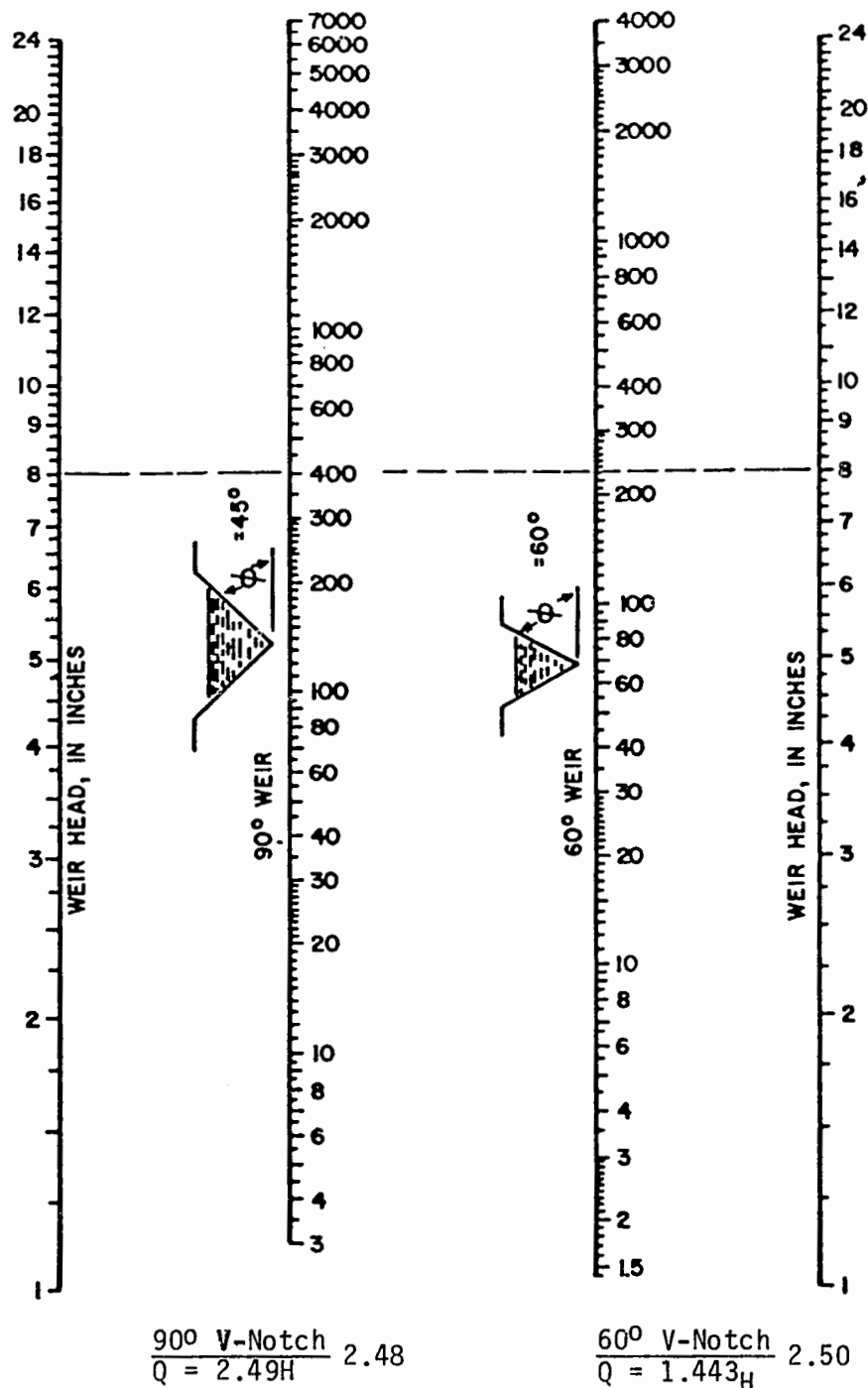
For shapes other than those mentioned above, head-discharge relationship must be established through field calibration using the salt-dilution (Section 3.4.3) or other methods.

Flow rates for 60° and 90° V-notch weirs can be determined from the nomographs in Figure 3.19. Figures 3.20a and 3.20b should be used for flow rates of V-notch weirs in conjunction with the Kindsvater-Shen formula; (6) the cone formula should be used only with fully contracted V-notch weirs. Flow rates for Cipolletti weirs can be obtained from Figure 3.21. Figure 3.22 is a nomograph for flow rates for rectangular weirs using the Francis formula; whereas Figure 3.23a and 3.23b should be used with the Kindsvater-Carter formula.

3.3.2.1.1 Criteria for Installing Standard Weirs

To achieve the best accuracy in flow measurement the following criteria should be met in installing standard weirs: (2)

1. The upstream face of the bulkhead should be smooth and in a vertical plane perpendicular to the axis of the channel.
2. The upstream face of the weir plate should be smooth, straight, and flush with the upstream face of the bulkhead.
3. The entire crest should be a level, plane surface which forms a sharp, right-angled edge where it intersects the upstream face. The thickness of the crest, measured in the direction of flow should be between 1 and 2 mm (about 0.03 to 0.08 in.) Both side edges of rectangular weirs should be truly vertical and of the same thickness as the crest.
4. The upstream corners of the notch must be sharp. They should be machined or filed perpendicular to the upstream face, free of burrs



where: Q = discharge in cubic feet per second H = head in feet

Figure 3.19 Nomograph for Capacity of 60° and 90° V-Notch Weirs (17)

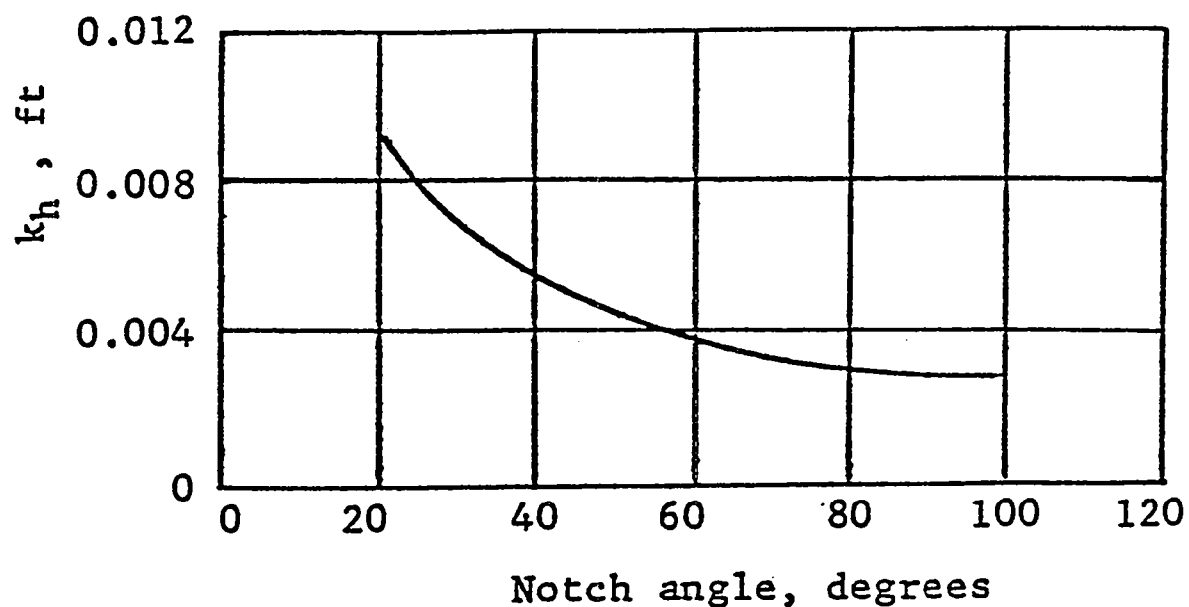


Figure 3.20a Value of k_h Kindsvater-Shen Formula for V-Notch Weir

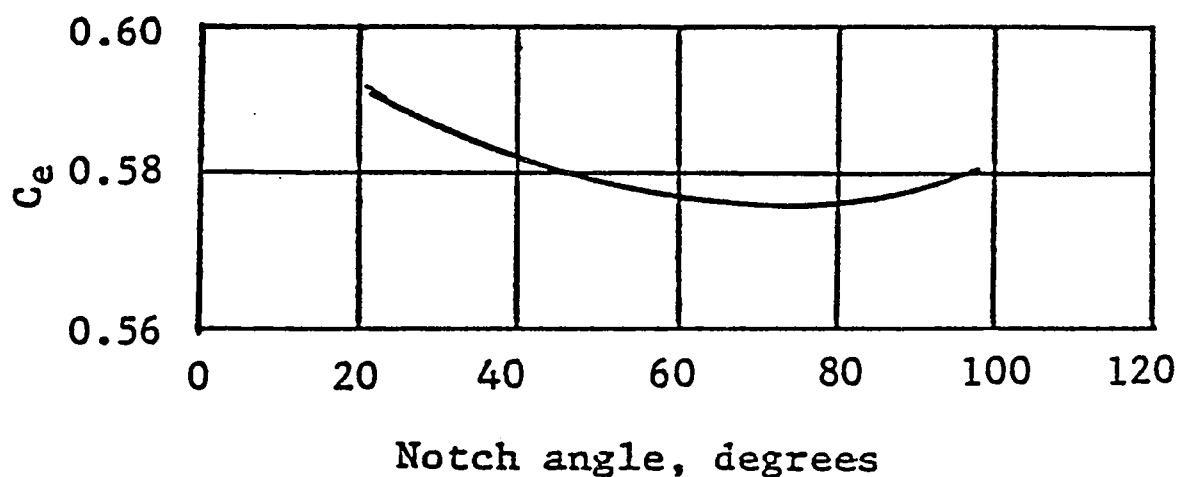


Figure 3.20b Value of C_e for Kindsvater-Shen Formula for V-Notch Weirs (20)

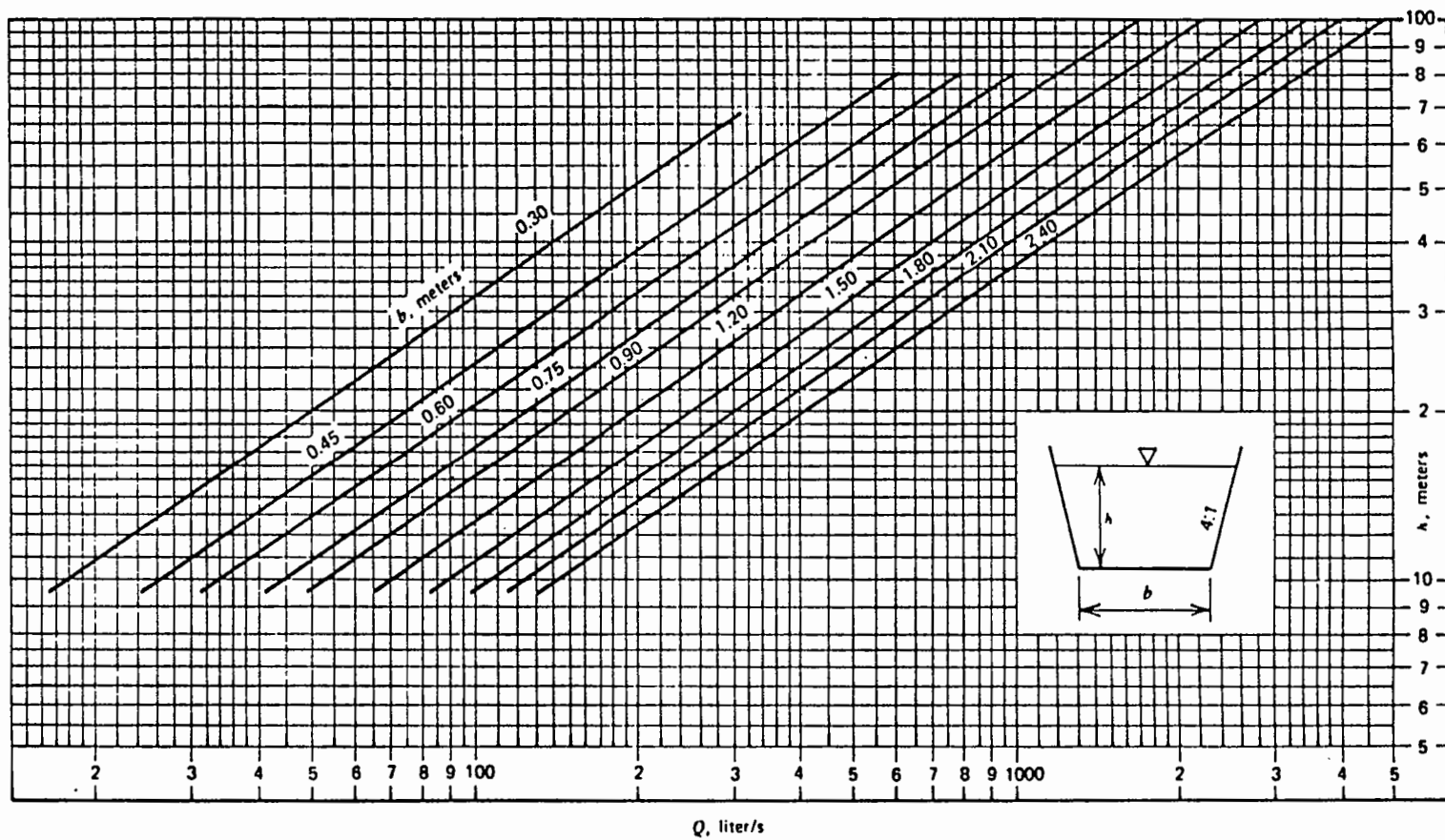
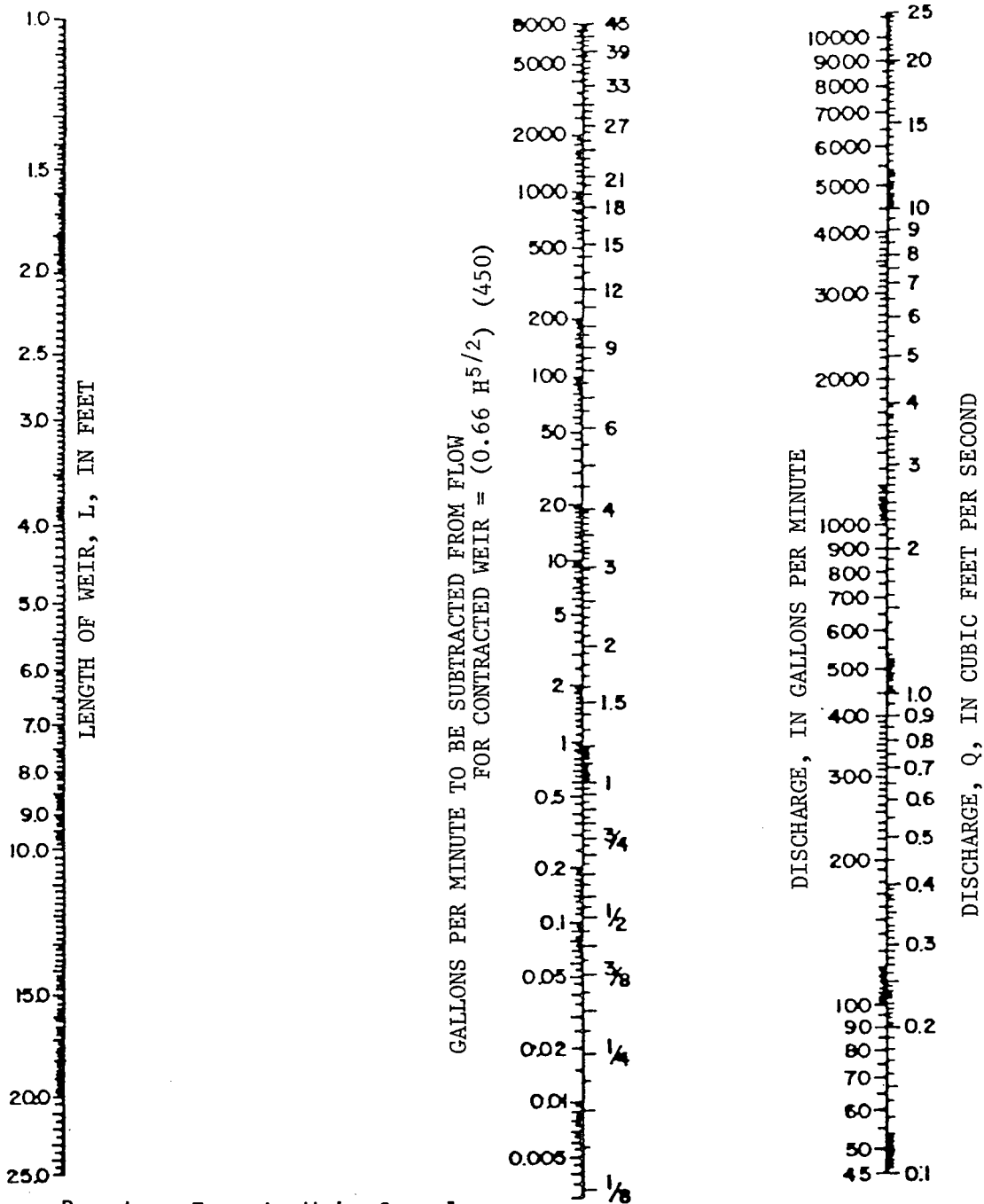


Figure 3.21 Flow Rates for Cipolletti Weirs (16)



Note: Based on Francis Weir formula
as follows:

or $Q = 3.33LH^{3/2}$ (for suppressed weir)
 $Q = 3.33(L-0.2H)H^{3/2} = 3.33LH^{3/2}$
 $-0.66H^{5/2}$ (for contracted weir with
two end contractions)

Where:

Q = discharge, in cubic
feet per second

L = length of weir, in
feet

H = head, in feet.

Figure 3.22 Nomograph for Capacity of Rectangular Weirs (7)

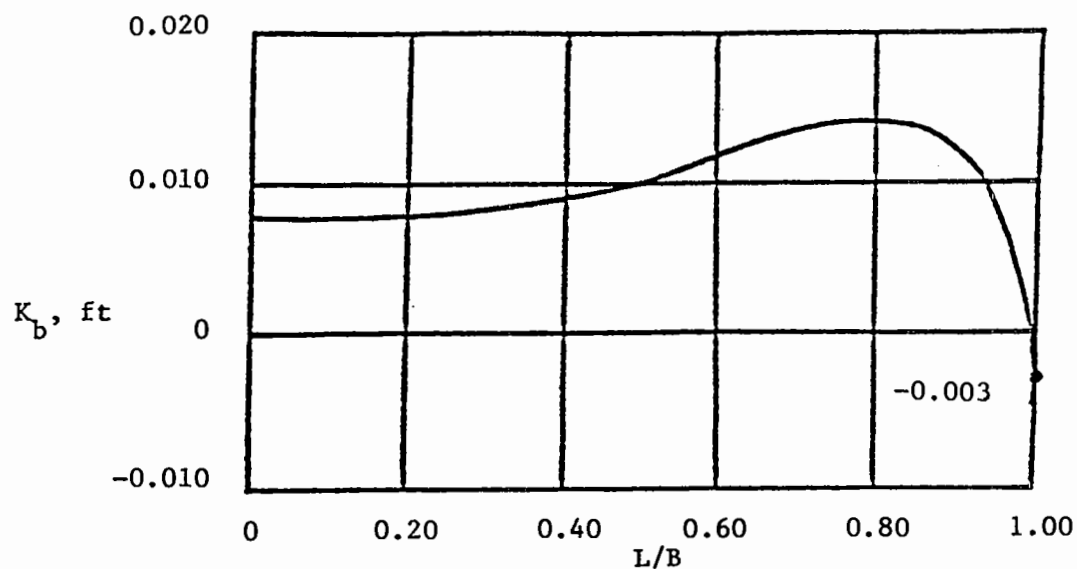


Figure 3.23a Value of K_b for L/B Ratio Kindsvater-Carter Formula for Rectangular Weirs (31)

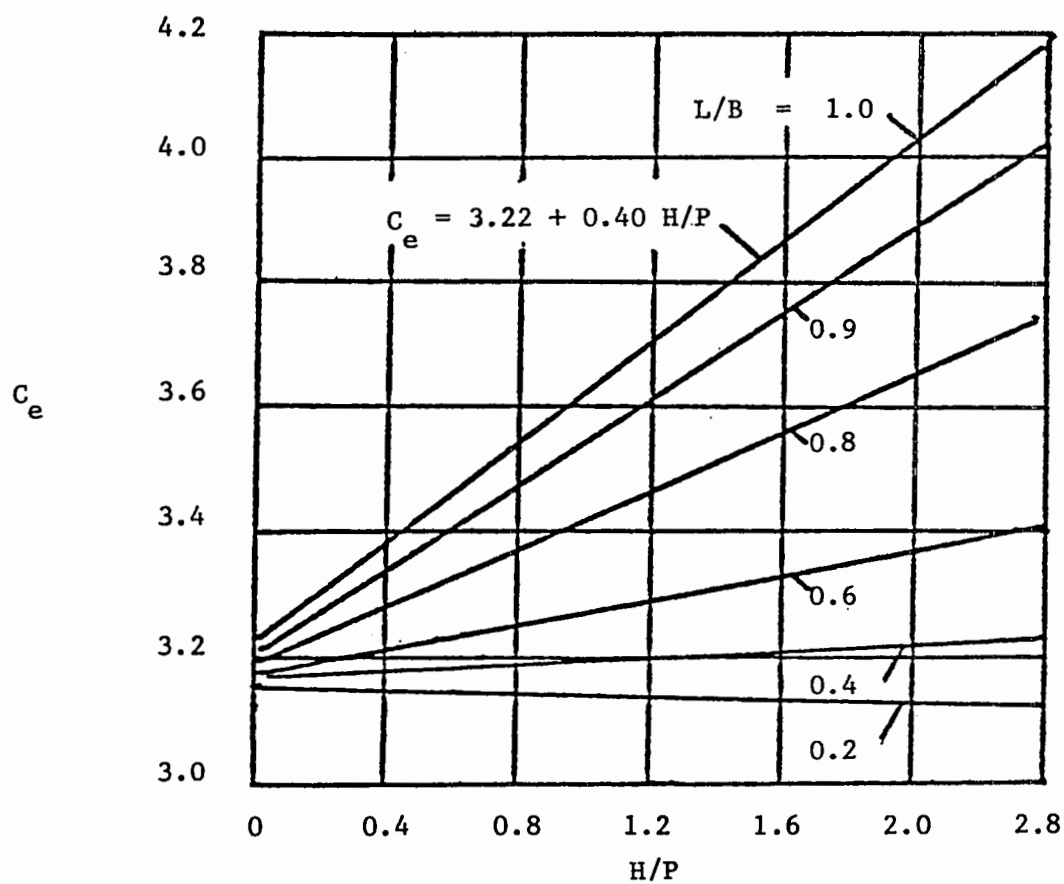


Figure 3.23b Value of C_e for H/P Ratio Kindsvater-Carter Formula for Rectangular Weirs (21)

or scratches, and not smoothed off with abrasive cloth or paper. Knife edges should be avoided because they are difficult to maintain.

5. The downstream edges of the notch should be relieved by chamfering if the plate is thicker than the prescribed crest width. This chamfer should be at an angle of 45° or more to the surface of the crest.
6. The distance of the crest from the bottom of the approach channel (weir pool) should preferably be not less than twice the depth of the water above the crest and in no case less than 0.31 m (1 foot).
7. The distance from the sides of the weir to the sides of approach channel should preferably be no less than twice the depth of water above the crest and never less than 0.31 m (1 foot). (Exception: suppressed rectangular weir for which sides of the notch should be coincident with the sides of the approach channel).
8. The overflow sheet (nappe) should touch only the upstream edges of the crest and sides.
9. Air should circulate freely both under and on the sides of the nappe.
10. The measurement of head on the weir should be taken as the difference in elevation between the crest and the water surface at a point upstream from the weir a distance of four times the maximum head on the crest.
11. The cross-sectional area of the approach channel should be at least 8 times that of the overflow sheet at the crest for a distance upstream from 15 to 20 times the depth of the sheet.
12. If the weir pool is smaller than defined by the above criteria, the velocity of approach may be too high and the staff gauge reading too low, and the head discharge relationship given in Section 3.3.1.1 will not hold good.

3.3.2.2 Flumes

In contrast to weirs which have a tendency to settle the suspended particles near their upstream side, most flumes have a self cleansing feature which makes them a preferred flow measuring device where sediment is a factor in the stability of the stage (head) discharge relation.

Flumes are comprised of three sections: a converging upstream section, a throat or contracted section, and diverging downstream section. The flume size is given by the width of the throat section.

Consider the following factors in the location of a flume:(2)

1. Do not install flume too close to turbulent flow, surging or unbalanced flow or poorly distributed velocity pattern.
2. Locate flume in a straight channel section having no bends upstream of the flume.
3. For convenience install flume at a location which is readily accessible, near the diversion point, and near the devices installed to control the discharge.

Some of the flumes commonly used as flow measurement devices are

described below.

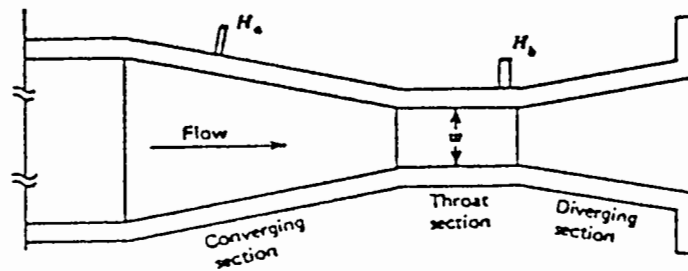
a. Parshall Flumes

Parshall flumes have been developed with throat width from 2.50 mm (1 inch) to 15.24 m (50 feet). The configuration and standard nomenclature for Parshall flumes is given in Figure 3.24. Strict adherence to all dimensions is necessary to achieve accurate flow measurement.

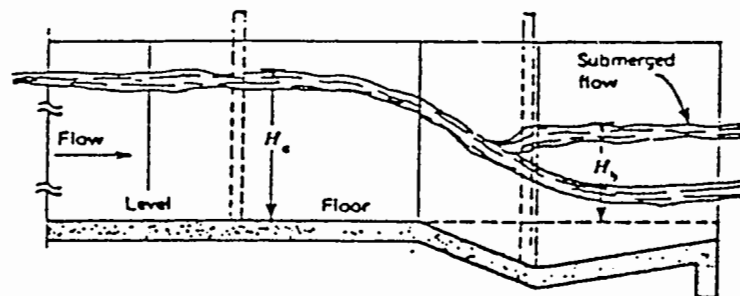
Flow through a Parshall flume may be either free or submerged. The degree of submergence is indicated by the ratio of the downstream head to the upstream head (H_b/H_a) - submergence ratio. The flow is submerged if the

submergence ratio is:

- greater than 0.5 for flumes under 0.076 m (3 inches) size
- greater than 0.6 for flumes 0.15 m - 0.23 m (6 inches - 9 inches) size
- greater than 0.7 for flumes 0.3 m - 2.44 m (1 to 8 feet) size
- greater than 0.8 for flumes bigger than 2.44 m (8 feet) size



a) Plan



b) Section

Figure 3.24 Parshall Flume Configuration and Nomenclature (16)

For a free flow in a Parshall flume of size (W), the upstream head (H_a) and discharge (Q) relationship is given by the general equation $Q = CWH^n$.

Table 3.7 gives the values of c, n, and Q, for different sizes (W) of the Parshall flume. Nomographs, curves or tables are readily available to determine the discharge from head observations. Flow curves are shown in Figure 3.25 to determine free flow through 0.07 m to 15.24 m (3 inches to 50 feet) Parshall flumes.(4)

For submerged conditions, apply a correction factor to the free flow determined using the relationship $Q = CWH^n$. These correction factors are given in Figure 3.26 for different sizes of the Parshall flume.

TABLE 3.7 FREE FLOW VALUES OF C AND N FOR PARSHALL FLUME
BASED ON THE RELATIONSHIP $Q = CWH^n$ (7)

Flume Throat, W	C	n	Max. Q, cfs
1 in	0.338	1.55	0.2
2 in	0.676	1.55	0.5
3 in	0.992	1.55	1.1
6 in	2.06	1.58	3.9
9 in	3.07	1.53	8.9
1 ft	4 W(*)	1.522W	16.1
1.5 ft	"	"	24.6
2 ft	"	"	33.1
3 ft	"	"	50.4
4 ft	"	"	67.9
5 ft	"	"	85.6
6 ft	"	"	103.5
7 ft	"	"	121.4
8 ft	"	"	139.5
10 ft	39.38	1.6	200
12 ft	46.75	1.6	350
15 ft	57.81	1.6	600
20 ft	76.25	1.6	1000
25 ft	94.69	1.6	1200
30 ft	113.13	1.6	1500
40 ft	150.00	1.6	2000
50 ft	186.88	1.6	3000

(*) W in feet

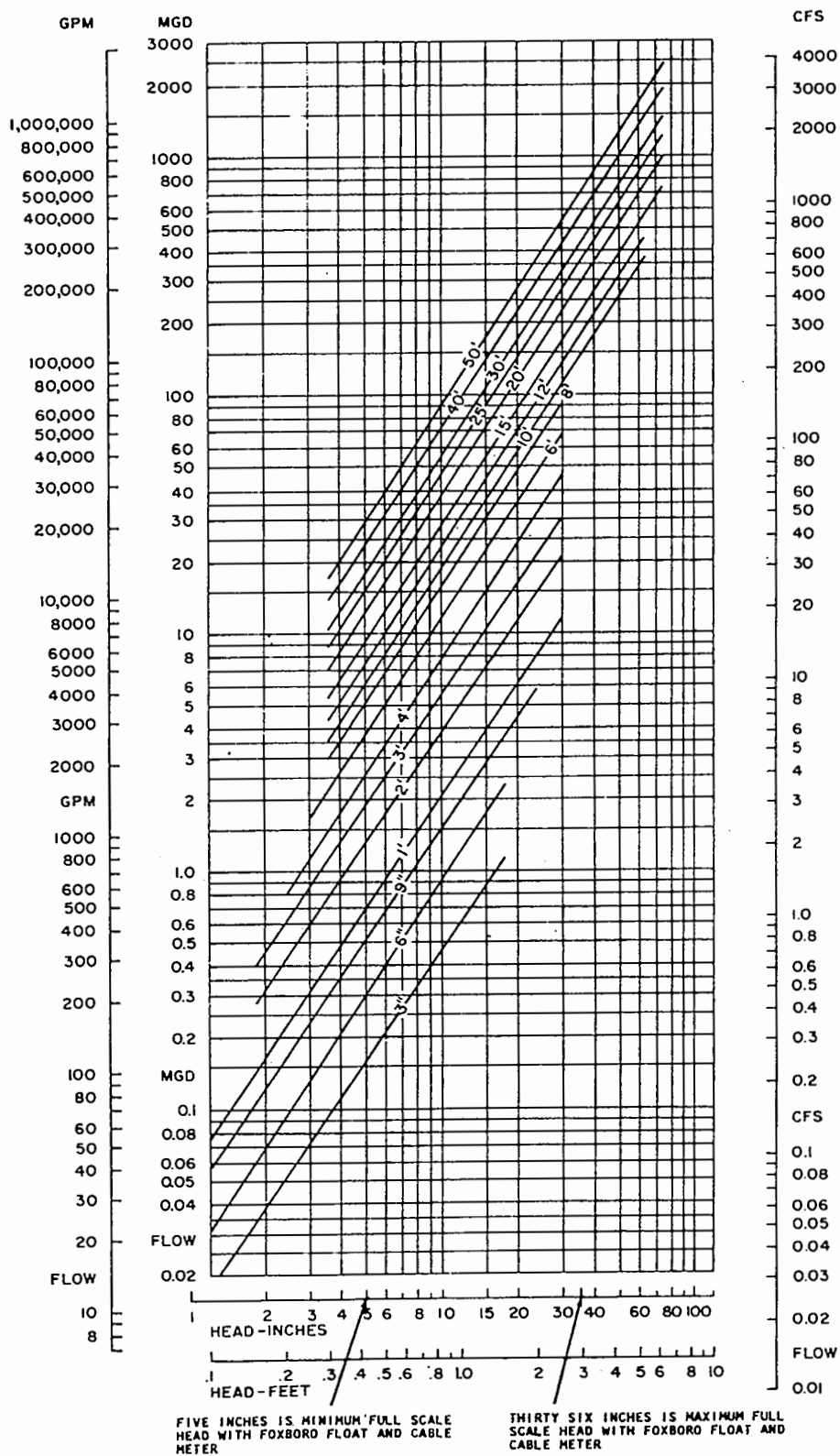
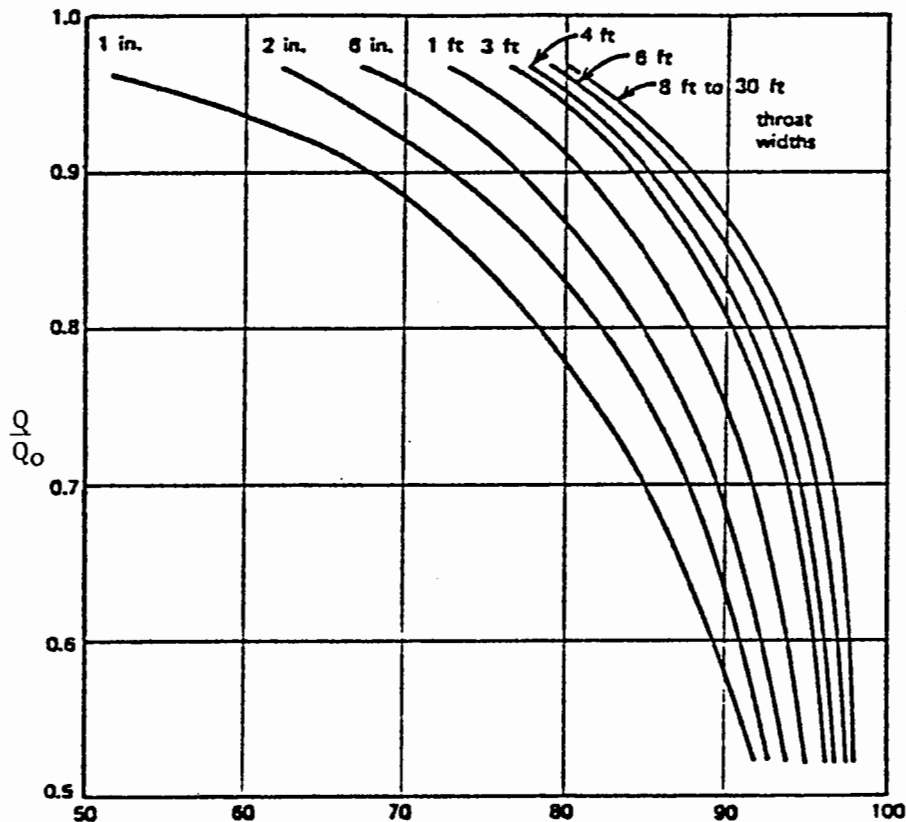


Figure 3.25 Flow Curves for Parshall Flumes (3)



Submergence, $\frac{H_a}{H_b}$, in percentage

Figure 3.26 Correction Factor for Flow Discharge Determination for Parshall Flumes (22)

b. Palmer Bowlus Flumes

Palmer Bowlus flumes are venturi flumes of a supercritical flow type designed to be inserted into an existing conduit with minimal site requirements other than sufficient slope. Figure 3.27 shows various types of Palmer Bowlus flumes. A laboratory study indicates that accuracies within 3% of the theoretical rating curve could be obtained at depths as great as 90% of the pipe diameter. (23) The chief advantage of Palmer Bowlus flumes over Parshall flumes is their ease of installation in existing

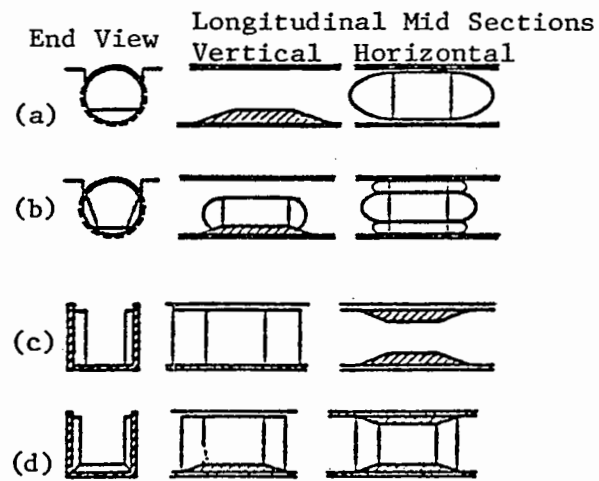


Figure 3.27 Palmer Bowlus Flumes (3)

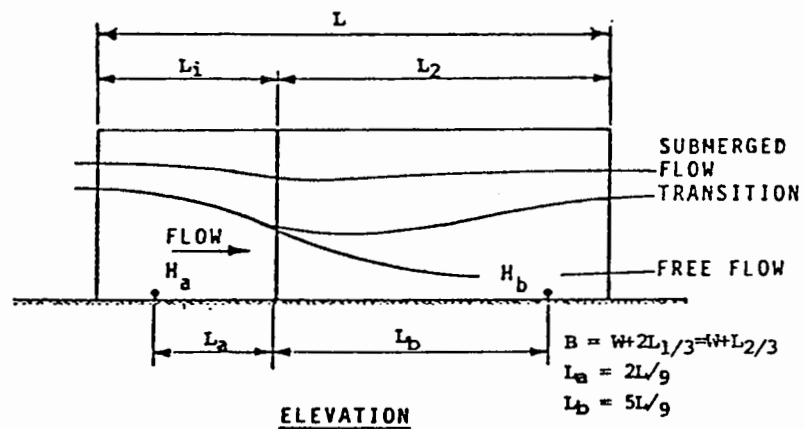
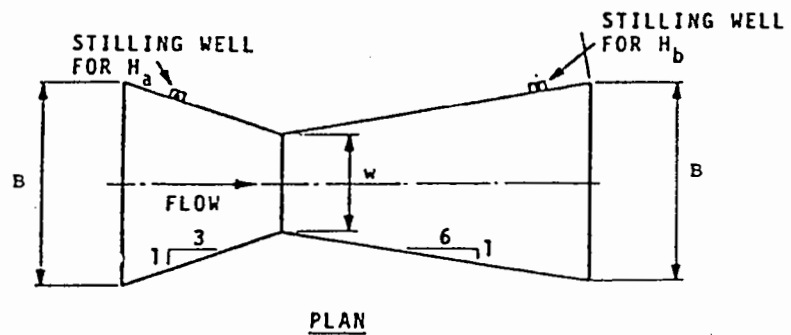


Figure 3.28 Rectangular Cut throat Flumes (5)

conduits and sewers. Standard Palmer Bowlus flumes are available to fit pipe sizes 15.2 cm (6 inches) to 2.4 meters (8 feet). A disadvantage of Palmer Bowlus flumes is that they have a small range of flow, about 20:1.

Diskin flumes, (24) an unconventional type of Palmer Bowlus flume, are portable devices but have limiting submergence, (H_b/H_a), between 0.75 and 0.85, and are not suited to trashy or debris laden flows.

c. Cut-throat Flumes

These are in a way modified Parshall flumes without throat section and flat bottom. (Figure 3.28). They are suitable for flat gradient channels; level flow and every flume size having the same wall lengths makes construction easy and less costly. Analytical and experimental background on these flumes can be found in reference 24.

d. Type HS, H, HL Flumes

These flumes are primarily used in irrigation channels and small water sheds. Figure 3.29 illustrates these flumes. Their main advantage is simplicity of construction, and they have a wide range of flow. Details on discharge ratings can be found in references 2 and 25. Their design incorporates the sensitivity of a sharp crested weir and the self cleansing feature of a Parshall flume.

e. Other Flumes

Trapezoidal flumes (Figure 3.30) have much larger capacities than rectangular flumes of the same bottom width. Two common types of flumes are: 1) trapezoidal flumes with bottom slope, and 2) trapezoidal critical depth flume. Accuracy of $\pm 2\%$ is claimed for trapezoidal critical depth flumes.

The San Dimas flume (Figure 3.31) was developed specifically to pass large amounts of sediment and debris. These flumes have the advantage that neither approach conditions nor disturbances upstream or downstream affect their discharge ratings. Their rectangular cross-section makes them less sensitive or accurate at low flows.

3.4 MISCELLANEOUS FLOW MEASUREMENT METHODS

3.4.1 Friction Formula

Measurements of channel or sewer bottom slope, depth of flow and flow velocity can be used to only roughly estimate the flow. The Manning formula is commonly used for estimating flow:

$$\frac{0.453}{n} R^{2/3} s^{1/2}$$

V = Average velocity, m/s

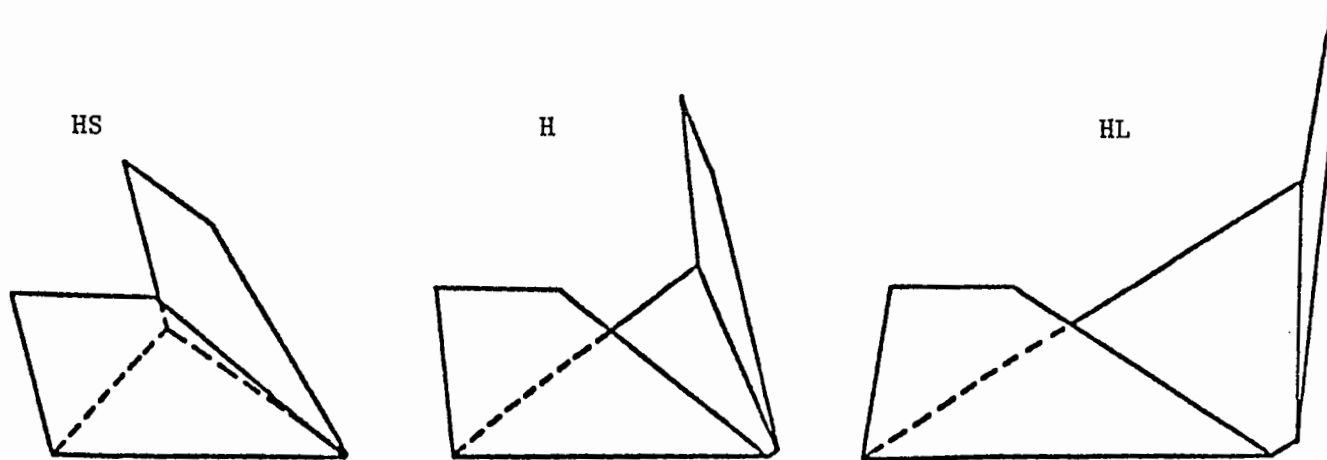


Figure 3.29 Type HS, H, and HL Flumes (5)

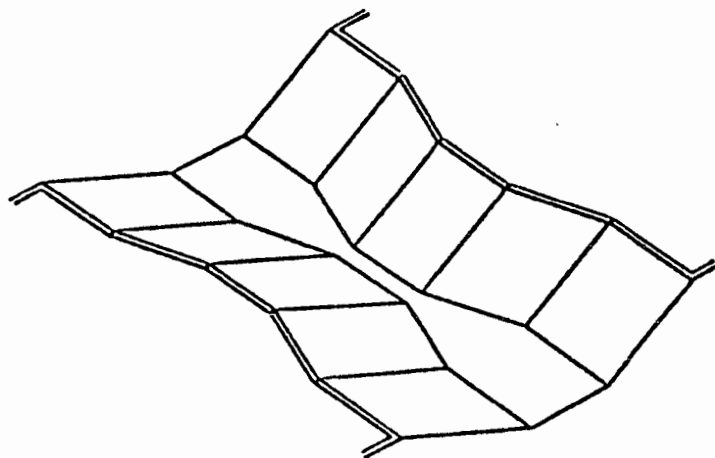


Figure 3.30 Trapezoidal Flume (5)

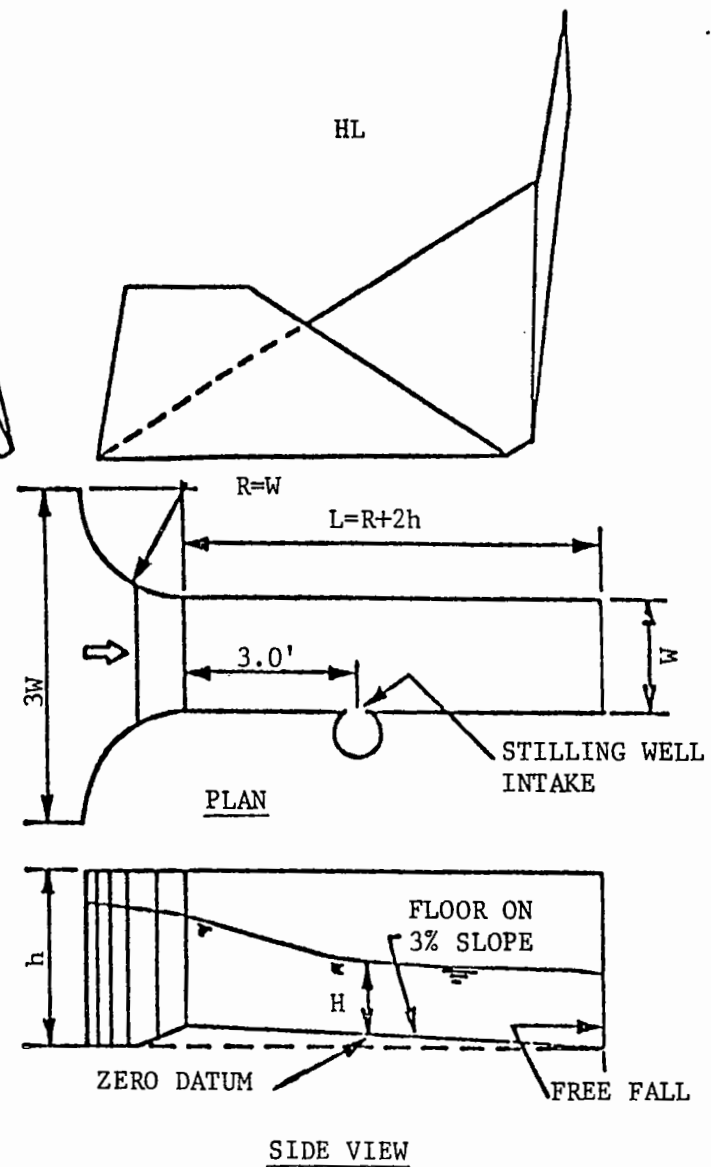


Figure 3.31 San Dimas Flume (5)

n = coefficient of roughness
 R = hydraulic radius, m $\frac{\text{cross sectional area of flow}}{\text{wetted perimeter}}$
 s = slope of energy grade line.

The Manning formula is widely used for the engineering design of sewers and channels. However, for flow measurement, its usefulness is limited for a number of reasons. It is difficult to assign an appropriate value to the roughness coefficient which varies with the channel or sewer material (concrete or brick), and the surface of the channel or sewer (new or old). For sewers, it varies also with the ratio of depth of flow to the depth when flowing full.

The other inaccuracy that may enter into the flow measurement is due to the slope of the energy grade line which is taken as the slope of the channel or sewer. However, these two slopes may or may not be identical. For various charts, tables and nomographs on the use of the Manning formula refer to reference 26.

3.4.2 Radioactive Tracer Techniques (7)

Radioactive tracer techniques measure the flow rate at the time of the measurement. These techniques require a license from Nuclear Regulatory Commission, are simple and relatively inexpensive, and the equipment is portable. These techniques require a section of the pipe or channel free of branch connections and turbulence at the injection point for thorough mixing of the tracer. The tracer must be a gamma-ray emitter, must be compatible with the flowing liquid, and must have a half-life longer than the duration of the test. Tracers generally used are salts of cesium-134, iodine-131, sodium 24, or gold-198. There are two methods of flow measurements by the radioactive tracers: 1) Two-Point Method and 2) Total-Count Method. Accuracies within 2% to 5% of the actual flow can be achieved using these methods.

a. Two-Point Method

This method uses the time interval for the surge of tracer to pass between two points separated by a determinable volume of the liquid. This time interval is determined by peaks on the chronological chart of a common amplifier-recorder connected to two G-M counters separated by a known or determinable volume of a section of a pipe. The schematics of the the arrangement of the test is shown in Figure 3.32.

b. Total- Count Method

The basic principle of the total-count method is that a well mixed finite quantity of radiotracer, A , passing through a measurement point will produce a total number of N counts on a Scaler connected to a Geiger counter fixed in or near the stream some distance downstream. The value of N is inversely proportional to the flow rate q and is directly proportional to A , the quantity of the tracer mixed:

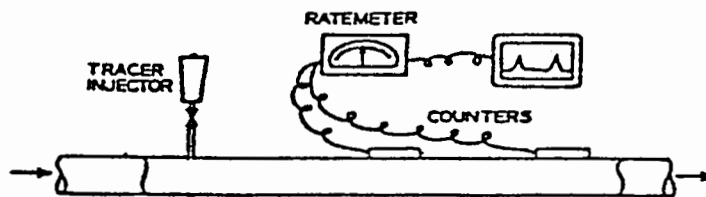
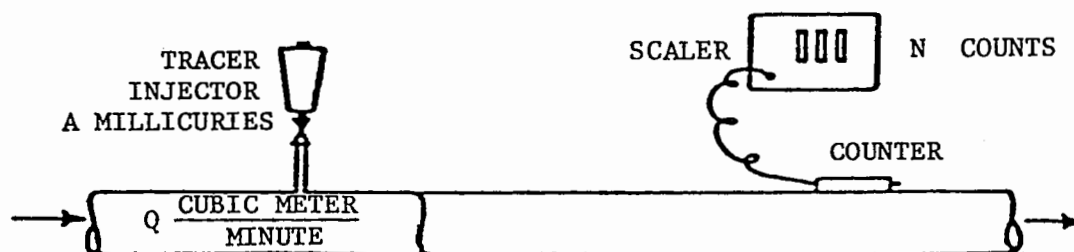


Figure 3.32 Schematic of Two Point Method (7)



$$F \frac{\text{COUNTS}}{\text{MINUTE}} / \frac{\text{MILLICURIES}}{\text{CUBIC METER}} = \frac{NQ}{A}$$

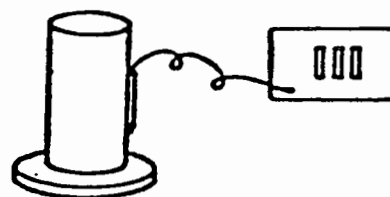


Figure 3.33 Schematic of Total Count Method (Upper Post) and arrangement for the Determination of F-Factor (Lower Post) (7)

$N = \frac{A F}{q}$, where F is a proportionality factor which is characteristic of the isotope, the counter, and geometrical relationship of the stream. Note that q is the flow rate at the tracer injection point.

The Total-Count Method gains versatility through the divided-stream principle: The same number of counts is obtained on the fraction or split flow as is obtained on the total flow. This allows one to measure a small fraction or bypass of the total flow.

To obtain accurate results, the numerical value of F must be determined in the laboratory by exposing the counter to a tracer solution in the same geometrical arrangement as in the field test, to find the counting rate that corresponds to a certain concentration of the tracer.

For example, if one desires to measure the flow of water/wastewater through a 30.4 cm (12 inch) pipe, take a 60.8 cm (2 foot) length of 30.4 cm (12 inch) pipe closed at one end, and fill it up with water/wastewater containing a known concentration of the radioactive tracer C to obtain millicuries per cubic meter (gallon). Strap the Geiger counter to the pipe and connect it to a scaler. Determine the number of counts per minute, n. Then the factor, G, for cubic meters per minute (gallons per min.) is:

$$F \text{ m}^3/\text{min} = \frac{n \text{ Counts per minute}}{C \text{ millicuries per cubic meter}}$$

Arrangement for the field measurement is schematically shown in Figure 3.33, upper post. To place the measurement, inject a known amount of tracer, A, either in a slug or gradually and record the total number of counts, N. Calculate the flow using the formula:

$$Q = \frac{A}{N} F \text{ substituting these values, and value of } F \text{ m}^3/\text{minute obtained above.}$$

The divided-stream principle is used in a modified technique, the sample-bucket technique, in which a fraction of total flow is passed through a bucket containing the counter. The factor F is determined with the actual bucket and the counter.

The procedure for measuring flow of a large open stream, such as a river, is accomplished by floating the counter any place in the flow downstream from the injection point. The value of F, is predetermined by submerging the counter at least 15.2 cm (6 inches) under the surface of liquid in a tank at least 1.2 m (4 feet) in diameter.

For better sensitivity a bundle of four counters connected in parallel and enclosed in lucite pipe is used.

3.4.3 Chemical Dilution (2)(6)(7)(27)

Chemical dilution technique also known as the salt dilution technique, is applicable to both the open channel and pipe flow. It does not require measurement of the stream dimensions or the measurements of fluid levels or pressures. The flow is determined by measuring the concentration of the chemical at two points downstream from the injection point. The following should be considered when using this technique for flow measurements in waters and wastewaters:

- . Turbulence at the point of injection of the chemical should assure thorough mixing (especially the lateral mixing) of the chemical in the field.
- . Flow in the channel or pipe should be steady.
- . Chemical used should meet the following requirements:
 - . Compatible with the fluid; no loss or deterioration of the chemical in the fluid.
 - . Non-toxic to plant and animal life.
 - . Easy and accurate quantitative detection at low concentration.
 - . Low cost of the chemical and the equipment.

Chemicals commonly used are lithium chloride (atomic adsorption analysis of lithium) and fluorescent dyes (fluorometer measurement) such as sodium fluorescein, Rhodamine B, Pontacyl Brilliant Pink B, and Rhodamine WT. However, use of sodium fluorescein is not recommended as it is easily affected by light and bacterial action. In waters/wastewaters with high suspended solids, there will be a pronounced loss of Rhodamine B dye. Recommended dyes, Pontacyl Brilliant Pink B and Rhodamine WT, are compared in Table 3.8.

TABLE 3.8 COMPARISON OF RHODAMINE B, RHODAMINE WT AND PONTACYL BRILLIANT PINK B DYES (27)

Factors	Rhodamine B	Rhodamine WT	Pontacyl Brilliant (Pink B)
pH 5-10	Stable	Stable	Stable
Absorption peak-visible light range	550 mu	556 mu	560 mu
Fluorescence peaks	570 mu	580 mu	578 mu
Suspended solids	Pronounced absorption	Low absorption	Low absorption

The chemical dilution technique is used in two ways: 1) continuous addition or 2) slug injection.

a. Continuous-Addition-of-Chemical-Method

In this technique the chemical of known concentration is added at a uniform rate to the stream and the dilution is determined after it has traveled downstream far enough to assure complete mixing. Samples collected at various points across the cross-section which show the same dye concentration will verify complete mixing.

$$A = q \frac{C_1 - C_2}{C_2 - C_0} \quad \text{where,}$$

A = stream discharge

C_0 = natural (or background) concentration of the chemical in the stream

C_1 = concentration of the chemical injected

C_2 = final concentration of the chemical at downstream sampling point

q = rate of injection of the chemical

b. Slug Injection Method

In this method, a known amount, S, of the chemical is added to the stream at a point sufficiently downstream to assure complete mixing. The concentration, \bar{C} , of the chemical during its time of travel, Δt , is determined by continuously sampling from the stream during the passage of the chemical wave and mixing this constant continuous sample into a single container to obtain an "integrated sample." The flow is determined by the

relationship $Q = \frac{S}{\bar{C}\Delta t}$ where,

Q = stream discharge

S = amount of chemical injected

\bar{C} = average concentration of chemical during its passage over a downstream point during time interval Δt

3.4.4 Water Meters

An estimate of the flow can be obtained from water meter readings when an instantaneous flow rate is not critical. This technique is used in a confined area, such as the industrial plant. Water meters should be certified periodically. When using the incoming and outgoing flow for an initial estimate of the flow rate, all changes in the water quantity that occur in various processes must not be overlooked. These changes may be due

to water actually consumed in the process, for example, cement manufacturer, conversion of quick lime to slaked lime, or the change of phase.

3.4.5 Measuring Level Change in Tank

In some instances the level change in a tank can be used to estimate flow. To accomplish this, the volume of the tank related to depth must be established; then the flow is allowed to enter and the level change with time is recorded. Figure 3.34 gives the relationship of depth to volume for various shapes of the tank.

3.4.6 Pump Rates

When other methods are not available for flow measurement and a pump is used in the system, the operating characteristics of the pump can be used to estimate flow. One method is to multiply the pumping time and the pump capacity at the discharge pressure as obtained from manufacturer's head curves versus flow. (28)

Another technique is to establish the pump's horsepower and determine the capacity from the manufacturer's curves. However, these techniques should be used only for estimates of flows.

3.4.7 Calibrated Vessels

Another technique useful for free falling water is to capture a known volume of water over a recorded time interval. The flow rate is then established for a specific time. More than one measurement is necessary to allow accurate estimates; the volume chosen should allow time for collection to be more than 10 seconds. (29)

3.5 SECONDARY DEVICES

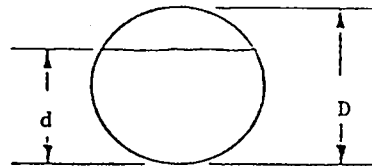
Secondary devices are the devices in the flow measurement system which translate the interaction of primary devices in contact with the fluid into the desired read-out or records.

These devices can be classified into two broad classes:

1. Non-recording type with
 - a. Direct read-out such as a staff gauge.
 - b. Indirect read-out from fixed points as in a chain, wire weight and float type.
2. Recording type, where the recorders may be graphic or digital. Examples of recording type devices are: float in well, float in flow, bubbler, electrical and acoustic.

The advantages and disadvantages of the various secondary devices are

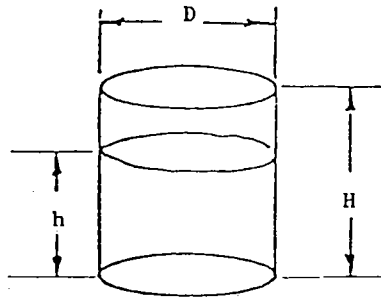
SPHERE



$$\frac{\text{Total Volume}}{V = 1/6 \pi D^3 = 0.523498D^3}$$

$$\frac{\text{Partial Volume}}{V = 1/3 \pi d^2 (3/2 D - d)}$$

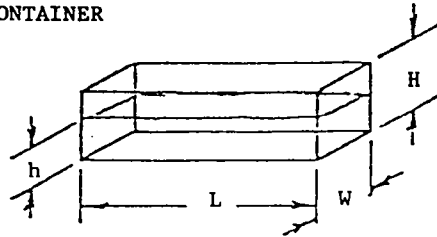
RIGHT CYLINDER



$$\frac{\text{Total Volume}}{V = 1/4 \pi D^2 H}$$

$$\frac{\text{Partial Volume}}{V = 1/4 \pi D^2 h}$$

ANY RECTANGULAR CONTAINER

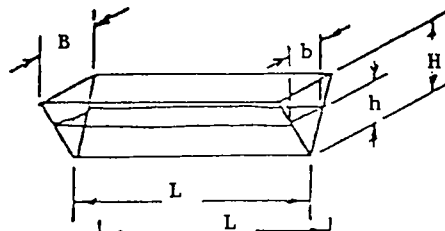


$$\frac{\text{Total Volume}}{V = HLW}$$

$$\frac{\text{Partial Volume}}{V = hLW}$$

TRIANGULAR CONTAINER

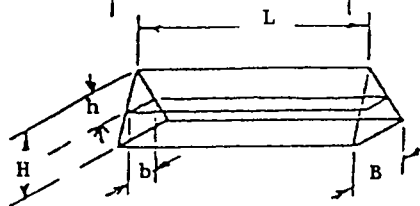
Case 1



$$\frac{\text{Partial Volume}}{V = 1/2 hBL} \quad (\text{Case 1})$$

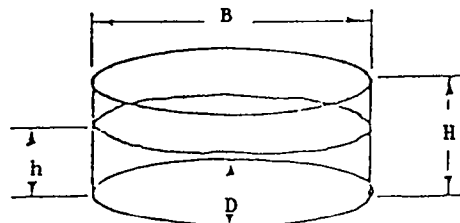
$$\frac{\text{Total Volume}}{V = 1/2 HBL}$$

Case 2



$$\frac{\text{Partial Volume}}{V = 1/2 L (HB - hb)} \quad (\text{Case 2})$$

ELLIPTICAL CONTAINER



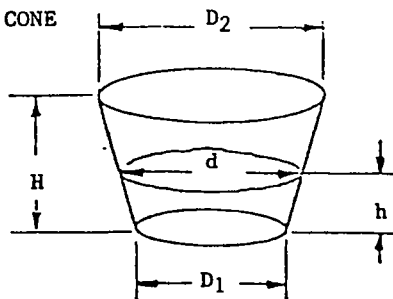
$$\frac{\text{Total Volume}}{V = \pi BDH}$$

$$\frac{\text{Partial Volume}}{V = \pi BDh}$$

Figure 3.34 Equations for Container Volumes

FRUSTUM OF A CONE

Case 1



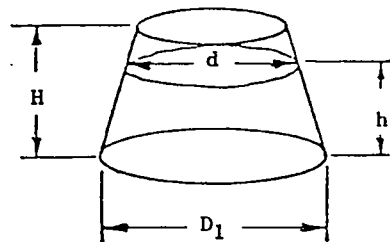
Total Volume

$$V = \pi/12 H (D_1^2 + D_1 D_2 + D_2^2)$$

Partial Volume

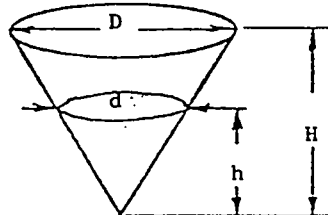
$$V = \pi/12 h (D_1^2 + D_1 d + d^2)$$

Case 2



CONE

Case 1



Partial Volume

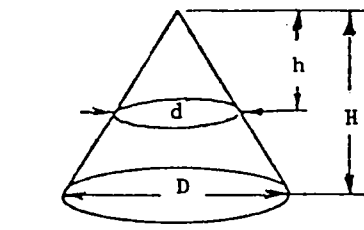
(Case 1)

$$V = 1/12 \pi d^2 h$$

Total Volume

$$V = 1/12 \pi D^2 H$$

Case 2



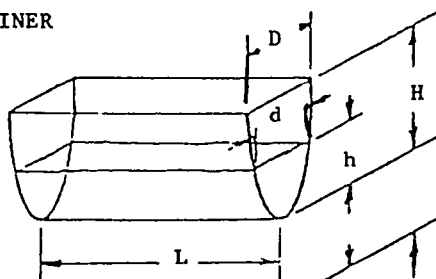
Partial Volume

(Case 2)

$$V = 1/12 \pi (D^2 H - d^2 h)$$

PARABOLIC CONTAINER

Case 1



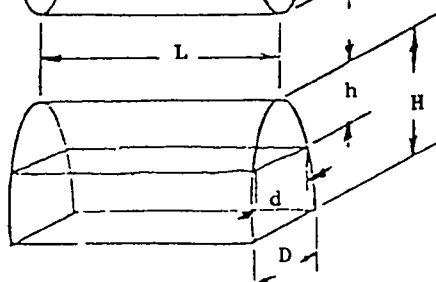
Partial Volume

$$V = 2/3 h d L$$

Total Volume

$$V = 2/3 H D L$$

Case 2



Partial Volume

$$V = 2/3 (H D - h d) L$$

Figure 3.34 (Continued)

given in Table 3.9 and relative comparison of primary and secondary open channel flow measurement devices is shown in Table 3.10. Table 3.11 compares various recording type secondary devices.

TABLE 3.9 ADVANTAGES AND DISADVANTAGES OF SECONDARY DEVICES

Device	Advantages	Disadvantages
Hook gauge or stage board	Common, accurate	Manual only, stilling well may be needed
Differential Pressure Measurement		
a. Pressure bulb	No compressed air source can be directly linked to sampler	Can clog openings, expensive
b. Bubbler tube	Self cleaning, less expensive; reliable	Need compressed air or other air source; Can't stand much abuse
Surface float	Inexpensive, reliable	In-stream float catches debris
Dipper	Quite reliable, easy to operate	Oil and grease will foul probe, possible sensor loss
Ultrasonic	No electrical or mechanical contact	Errors from heavy turbulence and foam

3.5.1 Non-recording Type Secondary Devices

3.5.1.1 Staff Gauge

A staff gauge, shown in Figure 3.35a, is usually a graduated enameled steel plate bolted to a staff. Care must be taken to install the gauges solidly to prevent errors caused by change in elevation of the supporting structure.

3.5.1.2 Hook Gauge

A hook gauge, shown in Figure 3.35b, is a modification to a staff gauge. The gauge (hook) is manually brought to the water surface and the water elevation read.

TABLE 3.10 RELATIVE COMPARISON OF PRIMARY AND SECONDARY OPEN CHANNEL
FLOW MEASUREMENT DEVICES (a)

Characteristic	Primary devices			Secondary devices				
	Channel-char's only (Manning formula)	Weir	Flume	Hook gauge stage board	Differential pressure	Float Device	Dipper	Ultra- sonic
Suitable for continuous measurement	+	+	+	-	+	+	+	+
Capability for sending signal to sample (flow- proportional sampling)	na	na	na	-	+	+	+	+
Need for stilling well	na	na	na	+	-	+	-	-
Low initial cost	3	2	1	3	2	3	1	1
Easy to install	na	2	1	3	2	1	2	2
High accuracy of measurement	1	2	3	2	3	3	3	3
Low maintenance (incl. cleaning)	3	1	3	3	2	2	3	3
Suitable for high solids wastewater	3	2	3	3	3	2	2	3
Low susceptibility to fouling (rags, debris, grease)	3	1	3	3	2	1	1	3
Wide flow range	3	2	3	+	+	+	+	+
Low headloss	3	1	3	+	+	+	+	+
Low auxiliary requirements (manpower, compressed air, AC power)	na	na	na	1	2	3	3	1

(a) na = not applicable

- = no or not suitable

+ = yes or suitable

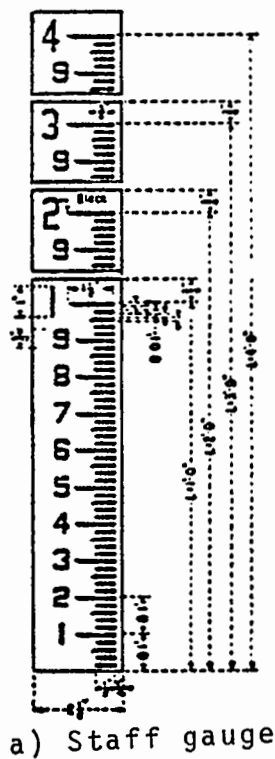
1 = fair frequently a problem

2 = good, sometimes a problem

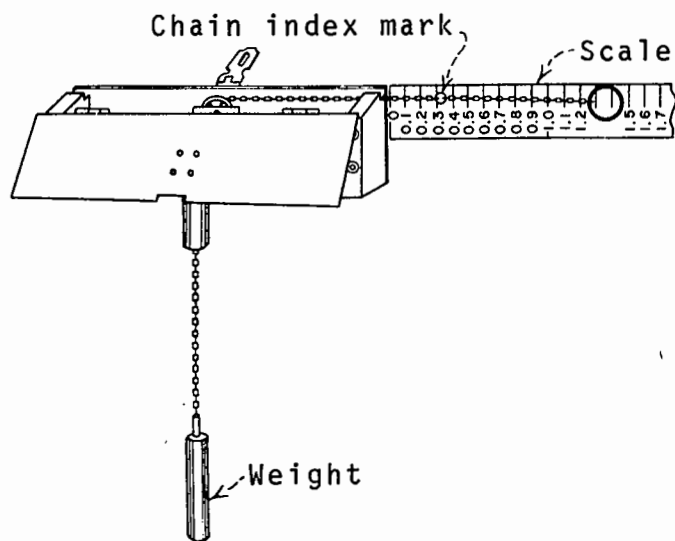
3 = excellent, seldom or never a problem

TABLE 3.11 COMPARISON OF RECORDING TYPE SECONDARY DEVICES

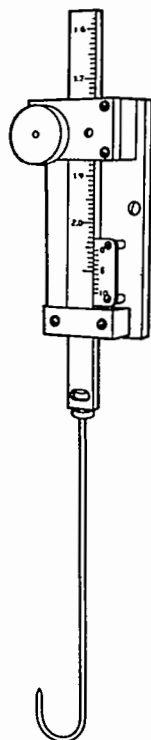
Features	Floating in Well	Float in Flow	Bubbler	Electrical	Acoustic
Stilling Well	Necessary	Not necessary	Not necessary	Not necessary	Not necessary
Sensing Flow Level	Indirectly	Directly	Flow level translated into air back pressure	Flow level translated into electrical property	Flow level translated into acoustic response
8 Purge System	Not required	Not required	May be required	Not required	Not required
Moving Parts	Presence of moving parts	Presence of moving parts	Absence of moving part	Absence of moving part where sensing element is physically in the flow. Present where probe is lowered for flow sensing.	Absence of moving parts



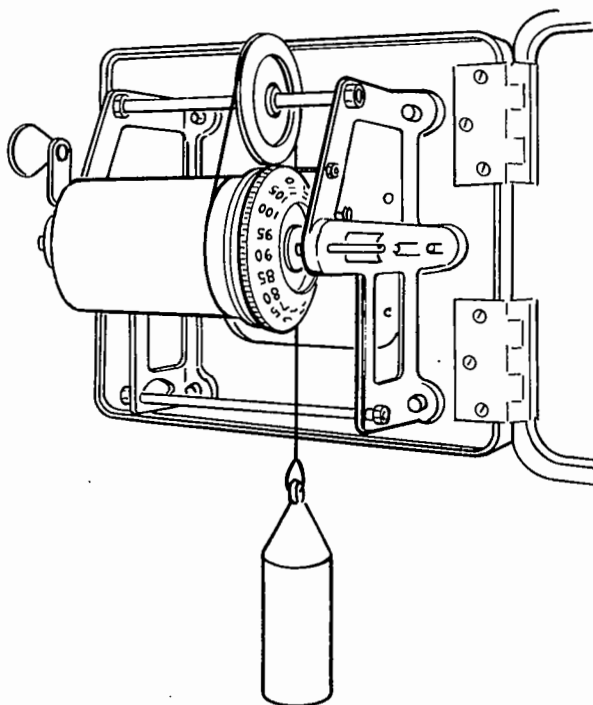
a) Staff gauge



c) Chain gauge



b) Hook gauge



d) Wire Weight gauge

Figure 3.35 Various Non-recording Type Secondary Devices

3.5.1.3 Chain Gauge

The chain gauge, shown in Figure 3.35c, is a substitute for the staff gauge and consists of a horizontal seal and a chain that passes over a pulley to fasten a hanging weight. Water level is indicated by raising or lowering the weight until it just touches the water surface. Sources of errors in the measurement are; settling of supporting structure, temperature changes, changes in length due to wear and wind action.

3.5.1.4 Wire Weight Gauge

Wire Weight gauge, shown in Figure 3.35d, is a modification of the chain gauge and uses a wire or small cable wound on a reel. The reel is graduated or a counter is used to give readings from a reference check bar of the water elevations to the tenths and hundredths of a foot.

3.5.2 Recording Type Secondary Devices

3.5.2.1 Float in Well

It essentially consists of a float (sensor weight) and a counter weight connected via a cable to a wheel which rotates as the float rises or falls with changes in the water level. The wheel is connected mechanically or electronically to the read-out or recorder. The float is installed in a stilling well.

3.5.2.2 Bubbler

In a bubbler, Figure 3.36, a pressure transducer senses the back pressure experienced by a gas which is bubbled at a constant flow rate through a tube anchored at an approximate point with respect to a primary device. This back pressure can be translated into water depth and subsequently related to discharge.

3.5.2.3 Electrical

These devices measure the change in a electrical property (capacitance or resistance) to sense liquid depth. The probe or sensor is part of an electrical circuit, and its behavior in a circuit is a function of its degree of immersion. Dippers touch the surface of the water and this completes a ground circuit; measurement of level is then accomplished by measuring the change in cable/reel rotation.

3.5.2.4 Acoustic

With acoustic devices, continuous measurement of liquid depth is accomplished by measuring the time required for an acoustic pulse to travel to the liquid-air interface and return. Of the two physical arrangements, liquid path and air path measurement, the air path arrangement is commonly used since installation is simplified, is independent of fluid velocity, and avoids any contact with the fluid.

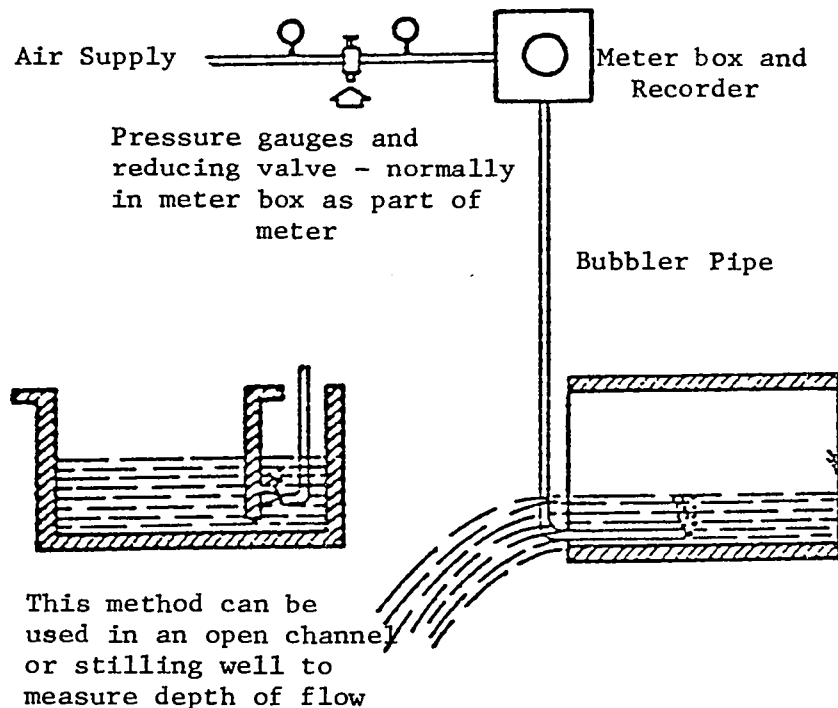


Figure 3.36 Bubbler

3.5.3 Errors in Flow Measurement (20)(30)

The final measurement accuracy of a system (primary and secondary devices included) depends on many factors.

3.5.3.1 Sources of Errors Related to the Primary Devices

Sources of errors described here are for weirs and flumes, but similar errors are associated with other devices:

Basic errors in the discharge/head tables or formulas. In many instances, the discharge tables, charts or formulas have been developed empirically. They show experimental relationships. Therefore, extrapolation beyond the range of observations from which they were developed can lead to serious errors.

- Faulty fabrication or construction. Erroneous Length: An error of 0.1 foot in the length of a rectangular or Cipolletti weir will cause an error of 1% in the flow measurement of a one foot weir. A corresponding error in 0.30 meter (one-foot throat width) flume will be 0.86% and that in a four foot flume 0.23%.
- Error due to transverse slope of weir crest. When the crest of the rectangular or Cippoletti weir is sloped, the common practice is to measure the head at the center of the crest. This leads to an error of

$$\frac{100S^2L^2}{32H^2} \% \quad \text{where:}$$

S = Slope of the weir crest

L = Length of the weir

H = Head at the center of the weir crest

This error can be reduced to an insignificant amount if the discharge is calculated as the difference of the discharges based on higher and lower heads on the weir crest.

- Stilling well not at a proper location. The head of the weir must be measured beyond the effect of the drawdown. For standard weirs the stilling well for the head measurement should be placed at a distance upstream of four times the maximum head on the weir. For Parshall flumes the locations of stilling wells for the head measurement bear a definite relationship with the throat width. Substantial errors in the field measurements have been traced to changes in the location or design of the stilling well entrance.
- Errors due to neglecting velocity of approach to weir. When the velocity of approach is greater than 0.5 fps it should be considered in the discharge formula. For a 0.2 feet head on the weir, this error for approach velocities of 0.15 m/s, 0.30 m/s, and 0.46 m/s (0.5 fps, 1.0 fps, and 1.5 fps) is 2.7, 9.8, and 20.8% respectively. This error is less when the head on the weir is greater. For a 0.30 m (1 foot) head, corresponding figures are 0.6, 2.2 and 4.7%. Use of the Kindsvater-Carter formula will help alleviate this error.
- The error due to the reduction of depth of the weir pool. The height of the weir, when less than twice the head on the weir, will introduce an error of 5.6, 2.7 and 1.5% for .06 meter (0.2 foot) head and 0.15, 0.30 and 0.61 meter (0.5, 1.0, 2.0 feet) height of the weir. A corresponding error of a 0.5 foot head will be 13.1, 6.4 and 3.4% respectively. This error can be corrected by using Rehbock's formula:

$$Q = \frac{2}{3} \sqrt{2g} L H^{3/2} \left(0.605 + \frac{1}{320H-3} + 0.08 \frac{H}{P} \right) \quad \text{or the}$$

Kindsvater-Carter formula. In a standard sized weir pool, this error can be minimized or eliminated by proper maintenance and

cleaning.

- . Weir blade sloping upstream or downstream. The error introduced is normally small. It becomes significant, however, if the face goes out of plumb by a few degrees.
- . Roughness of upstream face of weir or bulkhead. The roughness of the upstream face of weir or bulkhead can cause an increase in the discharge. The discharge is observed to increase by changing the roughness of the upstream face of the weir bulkhead from that of a polished brass plate to that of a coarse file for a distance of 30.48 cm (12 inches) below the crest. The increase ranges from 2% for 0.15 meters (0.50 foot) head to about 1% for 0.412 meter (1.35 foot) head.(30)
- . Aeration of the nappe. Insufficient aeration of the nappe will increase the discharge over the weir. It has been observed that for a drop in pressure under the nappe by 20.32 mm (0.8 inches) of water below atmosphere pressure, the discharge increased by 3.5% at 0.15 meter (0.5 foot) head and about 2.0% at 0.30 meter (1.0 foot) head.(30)
- . Other errors may be due to submergence of the weir, obstructions in the measuring section, changes in the viscosity and surface tension, and unstable flow at very low heads.

3.5.3.2 Errors in the Secondary Devices

- . Error due to incorrect zero setting of the head gauge. This error is of the same magnitude as the error for misreading the head.
- . Error due to misreading the head. Popular causes of this error are incorrect location of the gauge, a dirty head gauge, not using the stilling well, considerable fluctuations of the water surface and carelessness on the part of the reader. For 30.48 cm-121.9 cm (12-14 inch) Cipolletti and 90° V-notch weirs, a small error of 3.05 cm (0.1 foot) in reading will introduce an error approximately 7.5% in discharge results for the lower heads. For greater heads, the error is less.
- . The chart related errors are common to all the recording type devices.
These errors are the result of the variations in the chart due to humidity, paper expansion and shrinkage.
- . The error common to the totalizers is the variation in the speed of totalizer drive motors.
- . Other errors which are characteristics of particular secondary devices are:
 - . Float Devices (12)
The error due to a float lag which is similar to the "play" between gears. Once the index is set to the true water level while the water is rising, it will thereafter show the correct water level. For a falling water level however, the index will be above the true water level by the amount of the float lag as shown in Figure 3.37a. If the index is set at true water level at some intermediate point between rising and falling water levels, the index will be proportionately low by the amount of

the float lag for rising water levels and high a similar amount on the falling water level, as shown in Figure 3.37b. For recorders and indicators, float lag =

$$0.37 \frac{F}{D^2}, \text{ where } F = \text{force required to move the mechanism,}$$

ounces. D = diameter of the float, inches, and float lag in feet.

- The error due to line shift. For every change in the water level, there is a movement of float line from one side of the float pulley to the other. This change of weight changes the depth of floatation of the float, consequently the stylus deviates from the true water height by a small amount. This is dependent on the change in the water level since the last correct setting, and weight of the line used between the float and the counter weight.

$$\text{Error from line shift} = 0.37 \frac{P}{D^2} \Delta H \quad \text{where:}$$

P = weight per unit length of the line, ounces

D = diameter of the float, inches

ΔH = change in water level, feet and error from line shift, shift in feet.

If the error from line shift occurs when the counter weight is submerged, the error =

$$0.34 \frac{P}{D^2} \Delta H$$

- The error for the submergence of the counter weight is the result of the reduced pull on the float which leads to the increased depth of floatation. The error for the submergence is given by X .

$$\Delta X = \frac{C}{S_c W A} - \frac{P(L-2B)}{W A} \left(2 - \frac{1}{S_1} \right)$$

where:

C = the counter weight

S_c = specific gravity of the counter weight

W = weight of the float

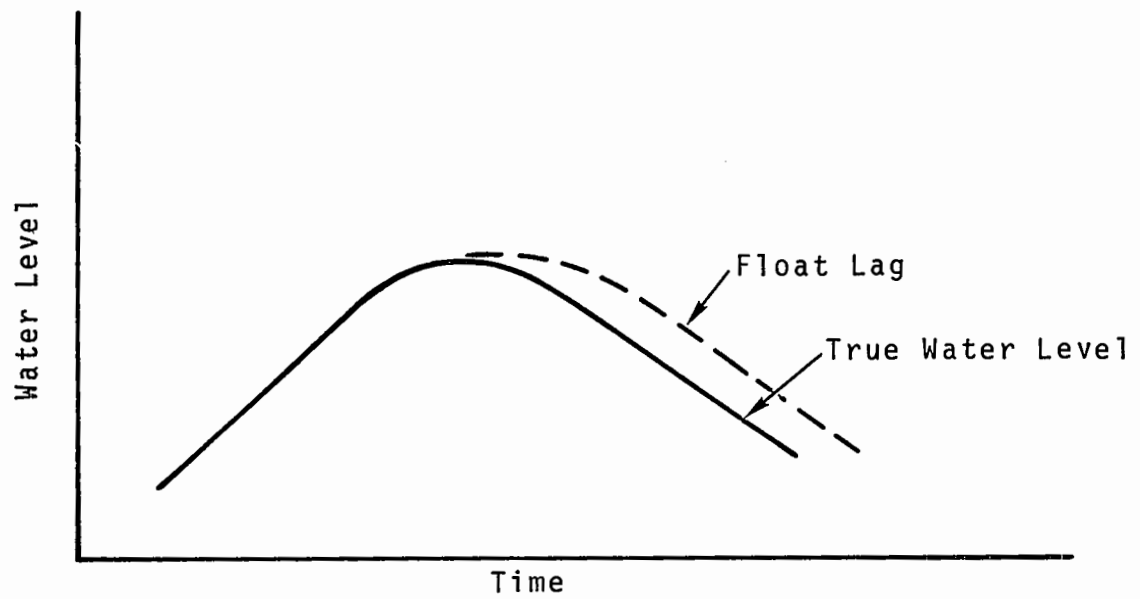
P = weight per unit length of the float line

L = total length of the float line from float to counter weight

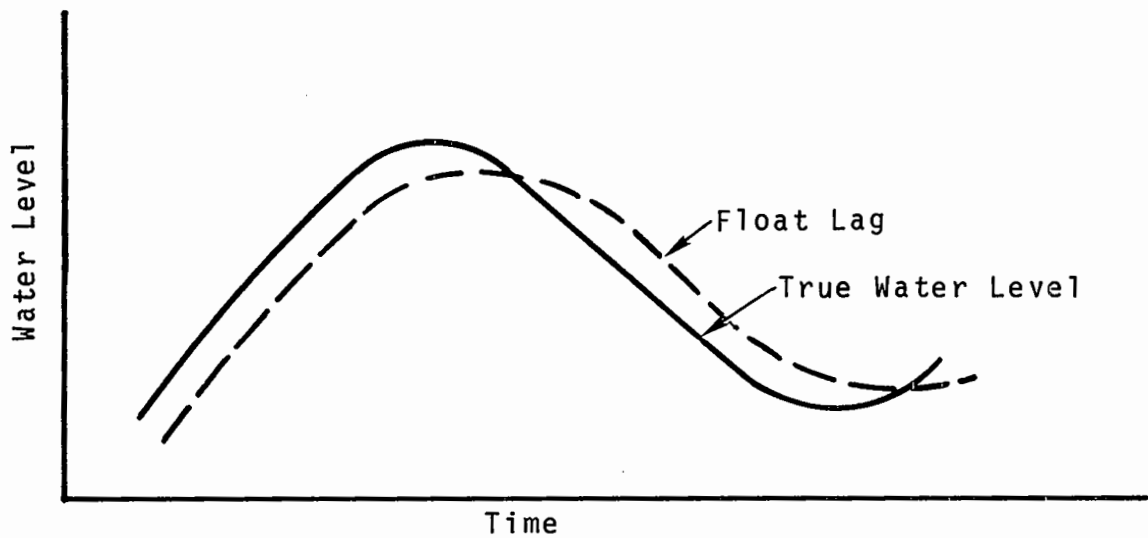
B = length of the float line, on the counter weight side

A = area of the float

S_1 = specific gravity of the float line



- a) Showing float lag when index is set to True Water Level while the water is rising



- b) Showing float lag when index is set at some intermediate point between rising and falling water levels

Figure 3.37 Float Lag (12)

- . The error due to fouling by trash or debris.
- . Bubbler

- . clogging of the exit and base of the bubble tube
- . aspiration effects due to velocity of flow
- . Errors due to temperature and aging
- . Errors due to hysteresis (lag effect)

- . Electrical

Main error is due to foam, floating oil or grease in the liquid.

- . Acoustic

The main errors are due to foam, highly turbulent-flow and false echo in restricted sites like manholes, meter vaults, etc.

3.5.3.3 Total Error in the Flow Measurement

Often, the total error in the flow measurement in a system is incorrectly taken as the sum of the errors in the primary and the secondary devices. However, the total error in the flow measurement is the square root of the sum of the squares of the individual errors. (31) Illustrative example is given below:

In the flow measurements through a 30.48 cm (12 inch) Parshall flume, the flow was $0.21 \text{ m}^3/\text{s}$ (7.41 cfs) at 457.20 mm (18 inches) of head. It was observed that there was a 3% error in the flow measurement for the Parshall flume. The error introduced by the use of a flow measurement formula was 1.5%. There was an error of 6.350 mm (0.25 inches) in the measurement of the throat. The error due to incorrect setting of zero was 3.175 mm (1/8 inches) and the error in the reading of the head was 3.18 mm (1/8 inches). Calculate the total percentage error.

$$\text{Percentage error in the head measurement (secondary device)} = X_n(e) = 100 \times \sqrt{\frac{\left(\text{error zero setting}\right)^2 + \left(\text{error head-reading}\right)^2}{(\text{Head})^2}}$$

$$X_n(e) = 100 \times \sqrt{\frac{(3.175)^2 + 3.175^2}{(457.20)^2}} = .982 = 1\% \text{ approximately}$$

$$\text{Percentage error in the primary device dimensions} \quad X_b(e) = 100 \times \frac{6.350}{304.80} = 2\% \text{ approximately}$$

Percent total error in the system =

$$X = \sqrt{\left(\text{Percent error of the flow}\right)^2 + \left(\text{Percent error of the formula}\right)^2 + \left(\text{Percent error of primary device}\right)^2 + \left(\text{Percent error of secondary device}\right)^2}$$

$$= \sqrt{3^2 + 1.5^2 + 2^2 + 1^2} = 4\% \text{ approximately}$$

3.6 REFERENCES

1. The American Society of Mechanical Engineers. Fluid Meters-Their Theory and Application, Report of the ASME Research Committee on Fluid Meters, 6th Edition, New York, NY 1971.
2. U.S. Department of Interior. Water Measurement Manual. Bureau of Reclamation, 2nd Edition, revised, 1974.
3. Associated Water and Air Resource Engineers Inc. Handbook for Industrial Wastewater Monitoring. U.S. Environmental Protection Agency, Technology Transfer, August 1973.
4. Buchanan, T.J. and W.P. Somers. Discharge Measurements at Gaging Stations. U.S. Geological Survey, Techniques of Water Resource Investigations, Book 3, Chapter A8, 1976.
5. Shelley, P.E. and G.A. Kirkpatrick. Sewer Flow Measurement-A State of the Art Assessment. U.S. EPA, EPA-600/2-75-027, November, 1975.
6. Kulin, Gerson and P.R. Compton. A Guide to Methods and Standards for the Measurement of Water Flow. U.S. Department of Commerce, National Bureau of Standards, Special Publication 421, May 1975.
7. American Petroleum Institute. Manual on Disposal of Refinery Wastes. Chapter 4, 1969 p. 1-26.
8. King, H.W. Handbook of Hydraulics. 4th Edition, McGraw Hill, 1954.
9. Strater, V.L. Fluid Mechanics, McGraw Hill, 1966.
10. Perry, R.H. and Chilton, C.H. Chemical Engineers' Handbook, 5th Edition, McGraw Hill, 1974.
11. American Society of Testing Materials. Annual Book of ASTM Standards, Part 31-Water. Philadelphia, Pennsylvania, 1967.
12. Leupold and Stevens Incorporated. Stevens Water Resource Data Book. 2nd Edition (revised), Beaverton, Oregon, 1975.

13. Kennard, J.K. Elementary Fluid Mechanics. 4th Edition, John Wiley & Sons, Inc., New York.
14. Blasso, L. Flow Measurement Under and Conditions. Instruments and Control Systems, 48, 2, pp. 45-50, February 1975.
15. Thorsen, T. and R. Oen. How to Measure Industrial Wastewater Flow, Chemical Engineering, 82, 4, pp. 95-100, February 1975.
16. Simon, Andrew. Practical Hydraulics. John Wiley & Sons, Inc. New York, 1976.
17. Smoot, G.F. A Review of Velocity-Measuring Devices. USDI, U.S. Geological Survey, Open File Report, Reston, Virginia, 1974.
18. Liu, H. Analysis of Integrating-Float Flow Measurement. Proceedings of the American Society of Civil Engineers, HY5, September 1968. pp. 245-1260.
19. Hajos, S. Neves. Verfahren zur Messung Kleiner Wassergeschwindigkeit. Zentralblatt der Bauverwaltung 24 (44), 1904 pp. 281-283.
20. Bos, M.G. Discharge Measurement Structures. Working group on Small Hydraulic Structures, International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands. 1076
21. Kindsvater, C.E. R.W. Discharge Characteristics of Rectangular Thin-Plate Weirs. Paper No. 3001, Transactions. ASCE Vol. 124, 1959.
22. Robinson, A.R. Simplified Flow Corrections for Parshall Flumes Under Submerged Conditions. Civil Engineering, ASCE. Sept., 1965.
23. Wells, E.A. and H.B. Gotass. Design of Venturi Flumes in Circular Conduits. American Society of Civil Engineering, 82, p. 23, April 1956.
24. Skogerboe, G.V., R.S. Bennett and W.R. Wallcer. Generalized Discharge Relations for Cut-Throat Flumes. Proc American Society of Civil Engineering, 98, IR4, pp. 569-583, December 1972.
25. Shelley, P.E. and G.A. Kirkpatrick. An Assessment of Automatic Sewer Flow Samplers. Office of Research and Monitoring, U.S. Environmental Protection Agency, EPA-600/2-76-065, Washington, D.C., December 1975
26. Water Pollution Control Federation, American Society Civil Engineers, Design and Construction of Sanitary and Storm Sewers, WPCF Manual No. 9, ASCE Manual and Reports on Engineering Practice No. 37, New York 1969.
27. Regpolo, J.A. L.E. Myers and K.J. Brust. Flow Measurements with Fluorescent Tracer. Proceedings of ASCE. HY5, 1966, p. 1-15.
28. Forester, R. and D. Overland. Portable Device to Measure Industrial Wastewater Flow. Jour. WPCF 46, pp. 777-778, April 1974.

29. Rabosky, J.G. and D.L. Koraido. Gauging and Sampling Industrial Wastewaters. Chemical Engineering, 80, pp. 111-120, January 1973.
30. Thomas, C.W. Errors in the Measurement of Irrigation Waters. Proc. Paper 1362, ASCE IR2, 1957. P. 1-24.
31. Mougenot, G. Weirs and Flumes. Water and Sewage Works, pp. 79-81, July 1974.

CHAPTER 4

STATISTICAL APPROACH TO SAMPLING

For every sampling program four factors must be established:

1. Number of samples
2. Sampling frequency
3. Parameters to be measured
4. Location(s) of sampling

These variables are usually established by the discharge permit requirements which may or may not be scientifically sound. When a new program is being initiated or the permit requirements need review, statistical methods and scientific judgment should be used to establish the best procedures.

This chapter explains various statistical terms and techniques and their applications to sampling. Each new concept is introduced with an example to illustrate its use. After the basic terms are defined and illustrated, statistical methods are introduced for analyzing data and determining the above four factors. These methods are also illustrated with examples.

4.1 BASIC STATISTICS AND STATISTICAL RELATIONSHIPS

Data representing a physical phenomenon are broadly classified as Continuous, such as temperatures measured constantly and recorded as a continuous curve; Discrete, such as temperatures recorded hourly; and as Deterministic, those capable of description by an explicit mathematical relationship or formula; or Non-deterministic, which are random. Due to water quality changes and the complexity of the processes affecting the water or wastewater characteristics, one cannot predict an exact value for a datum at a future instant in time. Such future data are random in character and are conveniently described in terms of probability statements and statistical averages rather than by explicit equations. However, long-term changes in water quality tend to have a functional character with random fluctuation components. Statistical evaluation techniques provide a tool with which to detect and quantify both the deterministic and random components of a water or wastewater quality record.

4.1.1 Statistical Sample Parameters - Definitions and Examples (1)

A wastewater stream is sampled once a week for a period of one year and the concentration of a certain parameter recorded. (See Table 4.1)

TABLE 4.1 WASTEWATER PARAMETER DATA

Week	Concentration (mg/L)	Week	Concentration (mg/L)
1	35.8	27	31.1
2	33.0	28	33.6
3	33.6	29	28.9
4	35.0	30	35.6
5	33.5	31	32.9
6	34.7	32	31.8
7	33.6	33	37.4
8	36.9	34	32.0
9	38.8	35	34.8
10	35.5	36	31.7
11	32.2	37	32.7
12	32.2	38	36.0
13	33.3	39	34.2
14	33.5	40	30.3
15	33.0	41	39.6
16	33.1	42	34.6
17	33.5	43	31.7
18	31.9	44	30.3
19	31.7	45	34.4
20	32.4	46	32.4
21	34.8	47	31.1
22	33.5	48	36.5
23	33.9	49	33.2
24	32.0	50	34.3
25	34.2	51	35.8
26	33.4	52	32.4

TABLE 4.2 WASTEWATER PARAMETER DATA IN DECREASING NUMERICAL ORDER

Observation #	Concentration (mg/L)	Observation #	Concentration (mg/L)
1	39.6	27	33.5
2	38.8	28	33.4
3	37.4	29	33.3
4	36.9	30	33.2
5	36.5	31	33.1
6	36.0	32	33.0
7	35.8	33	33.0
8	35.8	34	32.9
9	35.6	35	32.7
10	35.5	36	32.4
11	35.0	37	32.4
12	34.8	38	32.4
13	34.8	39	32.2
14	34.7	40	32.2
15	34.6	41	32.0
16	34.4	42	32.0
17	34.3	43	31.9
18	34.2	44	31.8
19	34.2	45	31.7
20	33.9	46	31.7
21	33.6	47	31.7
22	33.6	48	31.1
23	33.6	49	31.1
24	33.5	50	30.3
25	33.5	51	30.3
26	33.5	52	28.9

These data do not give much information as presented, so certain calculations are performed to give more meaning. Two things providing useful information about a set of data are: measures of central tendency, such as arithmetic mean and median; and measures of deviation, such as range, variance and standard deviation.

4.1.1.1 The Arithmetic Mean

The arithmetic mean or simply the mean is used to locate the "center" of a data set. It is defined to be the sum of all the observations divided by the number of observations (N):

$$\bar{X} = \frac{\sum_{i=1}^N X_i}{N}$$

where: X_i are the observations, with i ranging from 1 to N

N is the number of observations

$\sum_{i=1}^N$ is the operator "sum" of all values of the variable following it (in this case X_i) as i covers the integers from 1 to N .

$$\sum_{i=1}^N X_i = X_1 + X_2 + X_3 + \dots + X_N$$

In the above example (from Table 4.1), $X_1 = 35.8$, $X_2 = 33.0$, ..., $X_N = X_{52} = 32.4$;

$$\sum_{i=1}^N X_i = 35.8 + 33.0 + 33.6 + \dots + 35.8 + 32.4 = 1748.3; \text{ and so the mean,}$$

which is denoted \bar{X} (read "X-bar"), is:

$$\bar{X} = \frac{\sum_{i=1}^N X_i}{N} = \frac{1748.3}{52} = 33.6 \text{ mg/L.}$$

The mean can be greatly affected by extreme values. If in Table 4.2 the first observation is replaced by 396.0 the mean becomes:

$$\bar{X} = \frac{396.0 + 38.8 + 37.4 + \dots + 28.9}{52} = \frac{2104.7}{52} = 40.5 \text{ mg/L}$$

which is considerably greater than the former value of 33.6.

The mean is the most often used measure of the "center" of a data set.

4.1.1.2 The Median

The median of a set of data is the observation in the middle, that is, the number that is located such that half of the observations are less than it and half are greater. To find the median of a set of observations, arrange the data in numerical order as in Table 4.2.

If N is the number of observations in the ordered data set (in this case, N , is 52), then the median is defined to be the mean of the $\frac{N}{2}$ th and $\frac{N}{2} + 1$ st observations if N is even (between the 26th and 27th here, which would be 33.5) or the $\frac{N+1}{2}$ th observation if N is odd (that is with 15 ordered observations, the median is the 8th value).

The median is a good measure of the location of the center of a set of data because it is unaffected by extreme values, since if the largest observation were 396.0 instead of 39.6, the median would still be 33.5. Unfortunately, it does not make use of all the information contained in the data, but rather uses only the relative sizes of the observations.

4.1.1.3 The Range

In addition to knowing where the "center" of a data set is, it is useful to know how spread out the data set is. One indicator of the spread of a data set is the range, which is defined as the difference between the largest and the smallest values in the set. For example, in Table 4.2, the largest is 39.6 (#1) and the smallest is 28.9 (#52) and so the range is $R = 39.6 - 28.9 = 10.7$.

Like the median, the range is simple to compute, once the data are arranged in decreasing or increasing order, but does not use all the information in the data.

4.1.1.4 The Variance

The variance, which is the average of the squares of the deviations of the data from their mean, is another indicator of how spread out the observations are. To find the variance, subtract the mean from each observation, square each of these differences, sum the squared terms, then divide the sum by one less than the number of observations, or in symbols:

$$s_x^2 = \frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N - 1}$$

Table 4.3 shows how this is done: i is the week and X_i is the corresponding concentration.

$$\sum_{i=1}^{52} (X_i - \bar{X})^2 = \sum_{i=1}^{26} (X_i - \bar{X})^2 + \sum_{i=27}^{52} (X_i - \bar{X})^2 = 67.00 + 151.11 = 218.11(\text{mg/L})^2$$

$$\text{Variance} = S_X^2 = \frac{\sum_{i=1}^N (X_i - \bar{X})^2}{N - 1} = \frac{\sum_{i=1}^{52} (X_i - 33.6)^2}{51} = \frac{218.11}{51} = 4.28(\text{mg/L})^2$$

There is another formula for computing S_X^2 which will be given here without an example:

$$S_X^2 = \frac{\sum_{i=1}^N (X_i^2) - N(\bar{X}^2)}{N - 1}$$

This formula says to square each observation and sum the squares. Then multiply the square of the mean (found earlier) by the number of observations (N), subtract this from the sum of squares just computed, then divide by $N-1$. This formula involves fewer steps since there is only one subtraction, as opposed to N subtractions using the other method, and less time since there is just one pass through the data.

4.1.1.5 The Standard Deviation

The units of the variance are the square of the units of the mean and of the original data. That is, if the data are expressed in mg/L, the variance is in mg^2/L^2 . Because of this, the standard deviation, which is the square root of the variance, is more commonly used as a measure of dispersion. In our example, the variance, S_X^2 , is 4.28, and so the standard deviation is:

$$S_X = \sqrt{S_X^2} = \sqrt{4.28} = 2.07 \text{ mg/L}$$

Since the data are expressed as mg/L, the standard deviation is also in mg/L.

The mean (\bar{X}) and standard deviation (S_X) are actually only estimates of parameters known as the population mean (μ_X) and population standard deviation (σ_X), which are discussed in Appendix A.

An interesting and useful fact about these two numbers is that in a normally distributed population (which is discussed later and is a

TABLE 4.3 COMPUTATION OF THE VARIANCE

i	x_i	$(x_i - \bar{x})$	$(x_i - \bar{x})^2$	i	x_i	$(x_i - \bar{x})$	$(x_i - \bar{x})^2$
1	35.8	2.2	4.84	27	31.1	-2.5	6.25
2	33.0	-0.6	0.36	28	33.6	0.0	0.00
3	33.6	0.0	0.00	29	28.9	-4.7	22.09
4	35.0	1.4	1.96	30	35.6	2.0	4.00
5	33.5	-0.1	0.01	31	32.9	-0.7	0.49
6	34.7	1.1	1.21	32	31.8	-1.8	3.24
7	33.6	0.0	0.00	33	37.4	3.8	14.44
8	36.9	3.3	10.89	34	32.0	-1.6	2.56
9	38.8	5.2	27.04	35	34.8	1.2	1.44
10	35.5	1.9	3.61	36	31.7	-1.9	3.61
11	32.2	-1.4	1.96	37	32.7	-0.9	0.81
12	32.2	-1.4	1.96	38	36.0	2.4	5.76
13	33.3	-0.3	0.09	39	34.2	0.6	0.36
14	35.5	-0.1	0.01	40	30.3	-3.3	10.89
15	33.0	-0.6	0.36	41	39.6	6.0	36.00
16	33.1	-0.5	0.25	42	34.6	1.0	1.00
17	33.5	-0.1	0.01	43	31.7	-1.9	3.61
18	31.9	-1.7	2.89	44	30.3	-3.3	10.89
19	31.7	-1.9	3.61	45	34.4	0.8	0.64
20	32.4	-1.2	1.44	46	32.4	-1.2	1.44
21	34.8	1.2	1.44	47	31.1	-2.5	6.25
22	33.5	-0.1	0.01	48	36.5	2.9	8.41
23	33.9	0.3	0.09	49	33.2	-0.4	0.16
24	32.0	-1.6	2.56	50	34.3	0.7	0.49
25	34.2	0.6	0.36	51	35.8	2.2	4.84
26	33.4	-0.2	0.04	52	32.4	-1.2	1.44

26

$$\sum_{i=1}^{26} (x_i - \bar{x})^2 = 67.00$$

52

$$\sum_{i=27}^{52} (x_i - \bar{x})^2 = 151.11$$

TABLE 4.4 COMPUTATION OF THE COEFFICIENT OF SKEWNESS

i	$x_i - \bar{x}$	$(x_i - \bar{x})^3$	i	$x_i - \bar{x}$	$(x_i - \bar{x})^3$
1	2.2	10.648	27	-2.5	-15.625
2	-0.6	-0.216	28	0.0	0.000
3	0.0	0.000	29	-4.7	-103.823
4	1.4	2.744	30	2.0	8.000
5	-0.1	-0.001	31	-0.7	-0.343
6	1.1	1.331	32	-1.8	-5.832
7	0.0	0.000	33	3.8	54.872
8	3.3	35.937	34	-1.6	-4.096
9	5.2	140.608	35	1.2	1.728
10	1.9	6.859	36	-1.9	-6.859
11	-1.4	-2.744	37	-0.9	-0.729
12	-1.4	-2.744	38	2.4	13.824
13	-0.3	-0.027	39	0.6	0.216
14	-0.1	-0.001	40	-3.3	-35.937
15	-0.6	-0.216	41	6.0	216.000
16	-0.5	-0.125	42	1.0	1.000
17	-0.1	-0.001	43	-1.9	-6.859
18	-1.7	-4.913	44	-3.3	-35.937
19	-1.9	-6.859	45	0.8	0.512
20	-1.2	-1.728	46	-1.2	-1.728
21	1.2	1.728	47	-2.5	-15.625
22	-0.1	-0.001	48	2.9	24.389
23	0.3	0.027	49	-0.4	-0.064
24	-1.6	-4.096	50	0.7	0.343
25	0.6	0.216	51	2.2	10.648
26	-0.2	-0.008	52	-1.2	-1.728

52

$$\sum_{i=1}^{52} (x_i - \bar{x})^3 = 272.765$$

phenomenon which occurs quite frequently), 68.3% of the observations will fall within $\mu_x \pm \sigma_x$, 95.5% will be found within $\mu_x \pm 2\sigma_x$, and 99.7% within $\mu_x \pm 3\sigma_x$.

Since \bar{X} approximates μ_x and S_x approximates σ_x , these percentages will hold approximately for $\bar{X} \pm S_x$, $\bar{X} \pm 2S_x$ and $\bar{X} \pm 3S_x$.

4.1.1.6 Coefficient of Variation

This statistic provides a measure of the dispersion relative to the location of the data set, so that the spread of the data in sets with different means can be compared.

$$\text{Coefficient of Variation} = CV = \frac{S_x}{\bar{X}}$$

4.1.1.7 The Coefficient of Skewness

The coefficient of skewness is a measure of the degree of asymmetry of the data about its mean.

$$\text{Coefficient of Skewness} = k = \frac{N \sum_{i=1}^N (X_i - \bar{X})^3}{(N-1)(N-2)S_x^3}$$

$$\text{In our example, } k = \frac{52 (272.765)}{51 (50) 8.870} = .63 \text{ (see Table 4.4)}$$

A positive coefficient of skewness indicates high extreme values and as shown on pages 136 and 137, leads to a mean greater than the median.

4.1.2 Harmonic Variations (2)

The use of the statistical concepts discussed so far depends on the assumption that the data record is random. The identification and estimation of the transient variations of a wastewater monitoring record is extremely important. It reduces the standard deviation, thereby making estimators more reliable. The techniques used in identifying and evaluating these components are trend removal and time series analysis.

4.1.2.1 Trend Removal

A trend in a wastewater monitoring record can usually be detected graphically. Trends can be either linear (increasing or decreasing) or non-linear (exponential or logarithmic). A trend may be defined as any harmonic component whose period is longer than the record length. Trend removal is an important step in data processing. If trends are not removed, large distortions can occur both in further data processing and in conclusions on the probability distribution of the measured parameter. In many wastewater monitoring programs the evaluation or detection of the trend

is a desired result in itself.

The usual method for evaluating a trend is the least-square procedure which can be used if a random or harmonic component is superimposed on a linear trend such that:

$$X(t) = \hat{X}(t) + X'(t)$$

where $X(t)$ is the data record expressed as a function of time. In the Table 4.1 data, t is expressed in weeks, and so $X(1) = X_1 = 35.8$, $X(2) = X_2 = 33.0, \dots, X(52) = X_{52} = 32.4$.

$\hat{X}(t)$ is the linear trend.

$X'(t)$ is the random component.

In this case, the trend can be approximated by a straight line of the form

$$\hat{X}(t) = a + bt.$$

The coefficients a and b are computed by regression analysis and can be proven to be:

$$a = \frac{\sum t^2 \sum X(t) - \sum t \sum t X(t)}{N \sum t^2 - (\sum t)^2}$$

$$b = \frac{N \sum t X(t) - \sum t \sum X(t)}{N \sum t^2 - (\sum t)^2}$$

where: N = the number of samples.
 t = the sampling interval

\sum = is the equivalent to $\sum_{t=1}^N$ and means, "sum the following terms for $t=1$ through N ".

After removal of this linear trend, $\hat{X}(t)$, the new time series is:

$$X'(t) = X(t) - (a + bt)$$

Table 4.5 contains a data set with a linear trend. There follows an example of identifying and removing this trend.

It can be seen in Figure 4.1 that the data contain an upward trend and also a harmonic component. The trend is identified by finding $X(t) = a + bt$.

$$a = \frac{13685(104.90) - 595(2139.5)}{34(13685) - (595)^2} = 1.46$$

TABLE 4.5 DATA SET WITH LINEAR TREND

Data			Computation		
t	X(t)	tX(t)	t	X(t)	tX(t)
1	1.0	1.0	18	3.8	68.4
2	1.4	2.8	19	3.7	70.3
3	1.9	5.7	20	4.8	96.0
4	2.0	8.0	21	4.4	92.4
5	2.5	12.5	22	4.3	94.6
6	2.4	14.4	23	4.6	105.8
7	2.5	17.5	24	4.3	103.2
8	2.8	22.4	25	4.4	110.0
9	2.1	18.9	26	4.3	111.8
10	2.2	22.0	27	3.9	105.3
11	1.7	18.7	28	4.3	120.4
12	1.8	21.6	29	3.6	104.4
13	1.5	19.5	30	3.2	96.0
14	1.8	21.6	31	3.8	117.8
15	1.9	28.5	32	3.4	108.8
16	2.8	44.8	33	4.5	148.5
17	2.7	45.9	34	4.6	156.4

$$\sum_{t=1}^{34} t = 595$$

$$\sum_{t=1}^{34} t^2 = 13685$$

$$\sum_{t=1}^{34} X(t) = 104.90$$

$$\sum_{t=1}^{34} tX(t) = 2139.5$$

TABLE 4.6 ADJUSTED DATA SET OF TABLE 4.5

Computation			Adjusted Data		
t	$\hat{X}(t)$	$X'(t)$	t	$\hat{X}(t)$	$X'(t)$
1	1.6	-0.6	18	3.1	0.7
2	1.6	-0.2	19	3.2	0.5
3	1.7	0.2	20	3.3	1.5
4	1.8	0.2	21	3.4	1.0
5	1.9	0.6	22	3.5	0.8
6	2.0	0.4	23	3.6	1.0
7	2.1	0.4	24	3.7	0.6
8	2.2	-0.6	25	3.8	0.6
9	2.3	-0.2	26	3.9	0.4
10	2.4	-0.2	27	4.0	-0.1
11	2.5	-0.8	28	4.1	0.2
12	2.6	-0.8	29	4.2	-0.6
13	2.7	-1.2	30	4.2	-1.0
14	2.8	-1.0	31	4.3	-0.5
15	2.9	-1.0	32	4.4	-1.0
16	2.9	-0.1	33	4.5	0
17	3.0	-0.3	34	4.6	0

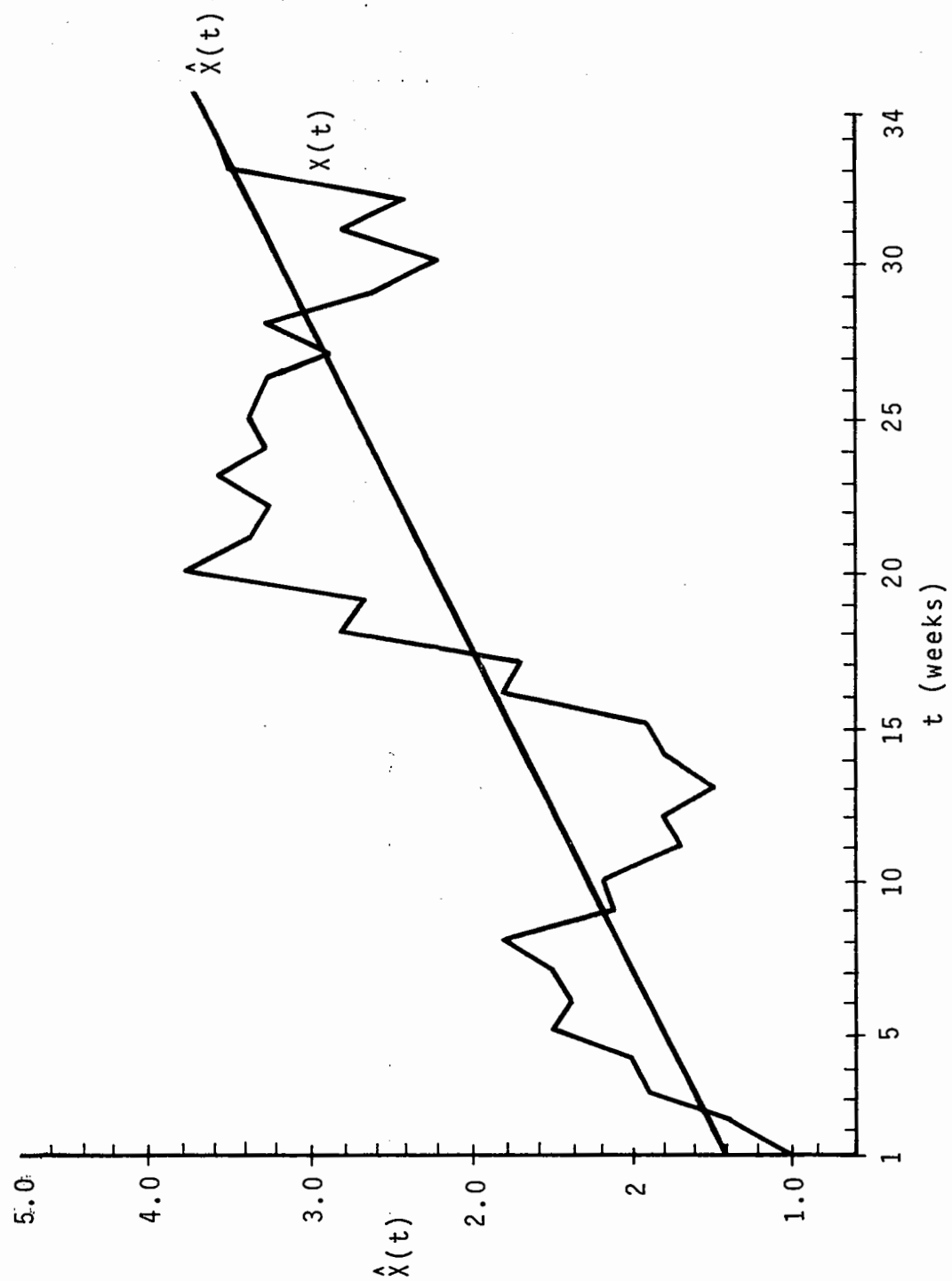


Figure 4.1 Series before removal of trend

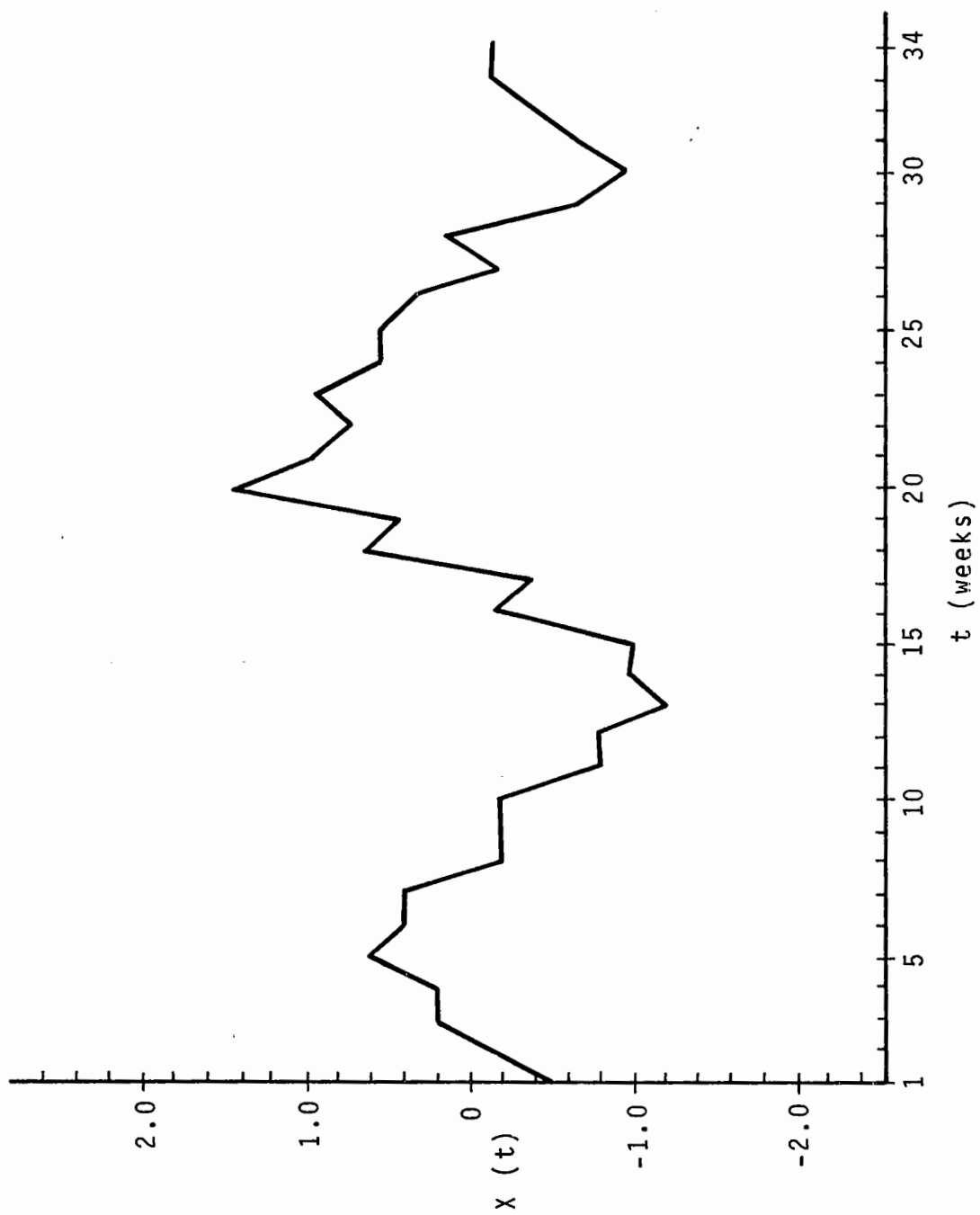


Figure 4.2 Series after removal of trend

$$b = \frac{34(2139.5) - 595(104.90)}{34(13685) - (595)^2} = 0.093$$

Therefore the line $X(t) = 1.46 + 0.093 t$. Since a linear trend is removed by subtraction, the new time series is:

$$X'(t) = X(t) - (a + bt) = X(t) - (1.46 + 0.093 t)$$

Table 4.6 lists the adjusted data and Figure 4.2 shows the series after the removal of the trend.

4.1.2.2 Time Series Analysis

Time series analysis is the most powerful method of analyzing a large volume of data, such as continuous records with high frequency of data acquisition. Since large amounts of data are required, time series analysis should not be used for short surveys or low frequency monitoring when limited amounts of data are available, or if part of the record is missing.

1. Auto-Covariance and Auto-Correlation Analysis

These functions describe the dependence of the values of the data at one time on the values at another time. An estimate of the auto-covariance function (acvf) between two observations $X(t)$ and $X(t + u)$, separated by a lag time, u , is given by:

$$c(u) = \frac{1}{N} \sum_{t=1}^{N-u} \{(X(t) - \bar{X})(X(t + u) - \bar{X})\}$$

where: N is the number of observations in the record

\bar{X} is the mean of the N observations

$c(u)$ is called the sample auto-covariance function of the time series, and is a function of the lag time, u .

Using the data in Table 4.5, we find that

$$\bar{X} = \frac{104.9}{34} = 3.1$$

and so, for $u = 4$,

$$c(4) = \frac{1}{34} \sum (X(t) - 3.1)(X(t + 4) - 3.1) = \frac{1}{34} (1.0 - 3.1)(2.5 - 3.1) + (1.4 - 3.1)(2.4 - 3.1) + \dots + (3.2 - 3.1)(4.6 - 3.1) = \frac{1}{34} (22.19) = .65$$

Since the acvf is a measure of the dependence between values separated by a specific time period, looking at $c(u)$ for various values of u will give information on this dependence. For example, in this set of data, $c(4) = 0.65$, $c(1) = 1.06$, and $c(10) = 0.12$. This shows that the auto-correlation decreases with increased lag time and is quite small when u reaches 10.

Notice that, except for N rather than $N-1$ in the denominator, $c(0) = S_x^2$, the sample variance. This says that the variance is just the serial-covariance of each observation with itself.

When the acvf is normalized by dividing by $c(0)$, it becomes the sample serial-correlation function (acf)

$$\gamma(u) = \frac{c(u)}{c(0)}$$

which is an indicator of how much one observation is dependent on those around it. It gives a visual picture (when plotted against the lag, u , between points) of how the dependence damps out as the lag increases. This graph is called the auto-correlogram. Figure 4.3 is the auto-correlogram for the data in Table 4.5. The fact that the curve in Figure 4.3 is somewhat like a sine wave is reflected in the auto-correlation, which begins to show negative correlation after u passes 11. For purely random data the acf would approach zero as u increases. A periodic component in the record would result in a periodic auto-correlogram with period similar to that of the original data. The principal application of the acf is to establish the influence of values at any time over values at a later time. It provides a tool for detecting deterministic data which might be masked in a random background.

2. Variance Spectral Analysis

In the analysis of time series, the "variance spectrum" more commonly known as "power spectrum" is a basic tool for determining the mechanism generating an observed series. The power spectrum is just the Fourier Transform of the theoretical acvf, $\gamma(u)$, and so is defined, as a function of frequency f ,

$$\text{by} \quad \Gamma(f) = \int_{-\infty}^{\infty} \gamma(u) \cos(2\pi fu) du$$

$$\text{where} \quad \gamma(u) = E \{ (X(t) - \bar{u}) (X(t+u) - \bar{u}) \}.$$

(The expectation operator E is defined in Appendix A).

By definition (Section 4.1.1), variance is a measure of the dispersion of observations about their mean value. This dispersion may result from purely random fluctuations (noise) in the observed data as well as from deterministic (non-random) fluctuations. These deterministic fluctuations may be the result of trends (linear) as well as periodic components in the record. Spectral analysis is a useful tool for the analysis of data records in which both random and deterministic fluctuations may be present as it allows its user

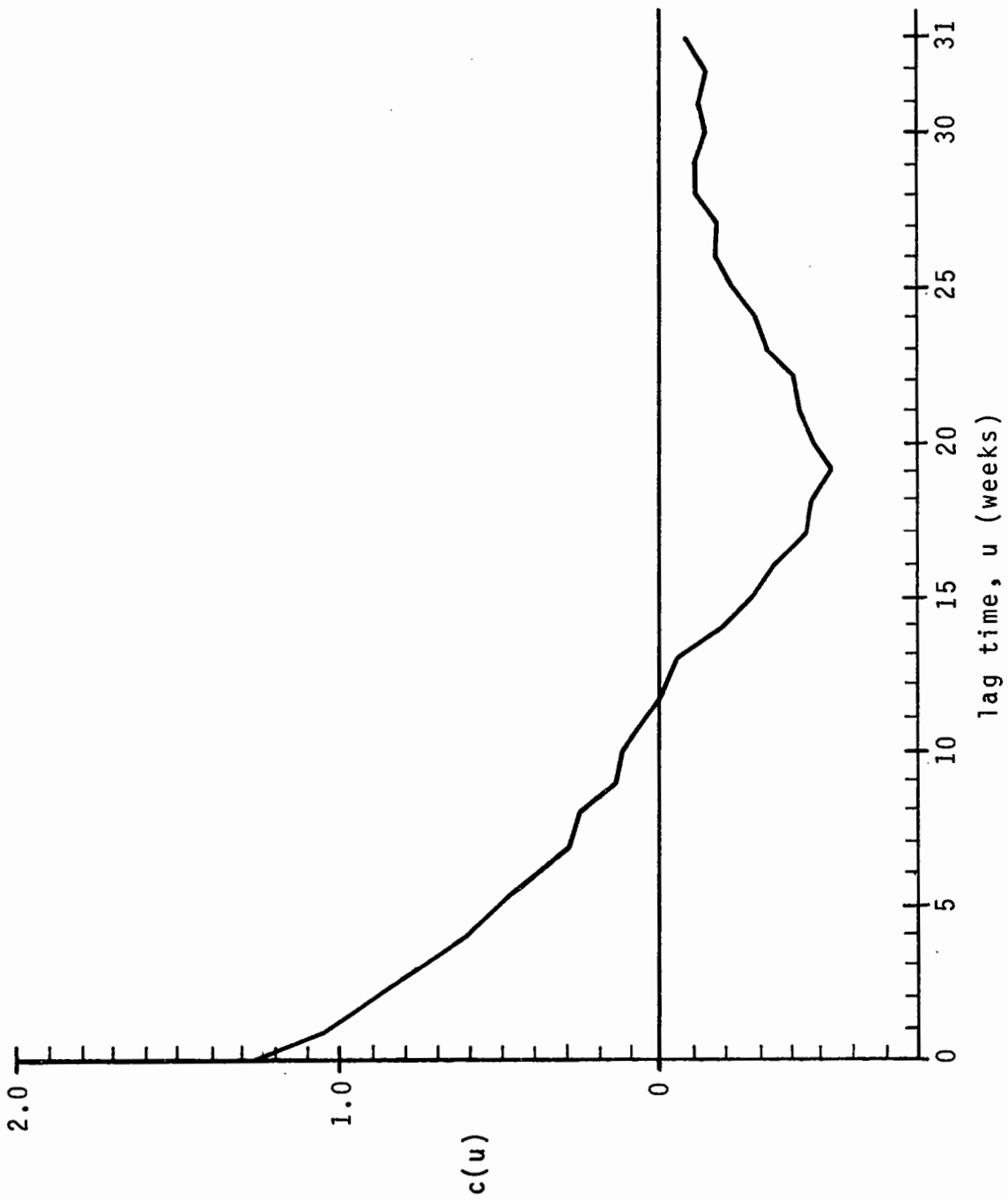


Figure 4.3 Serial-correlogram

to separate these two types of fluctuations.

In spectral analysis of a data record, which ideally but not necessarily should be continuous, the power spectrum $\Gamma(f)$ of the series is plotted against frequency f . Figure 4.4 shows six hypothetical data records and their corresponding power spectra.

Figure 4.4a shows a record on which all observed values are equal and therefore equal to their mean. Their variance is zero and therefore the power spectrum plot is zero at all frequencies.

Figure 4.4b shows a record with a linear trend. The variance in this record is a result of the time dependent linear trend in the record. There is no random or periodic dispersion about the mean, consequently all of the variance (or power) spectrum is concentrated at the zero frequency.

Figure 4.4c shows a record exhibiting periodic harmonic fluctuations with frequency f_1 . The variance in this record is a result of the harmonic fluctuation of frequency f_1 about the mean. All the power spectrum is concentrated at the f_1 frequency.

Figure 4.4d shows a record with purely random fluctuations (white noise) about a constant mean value. The variance in this record is a result of these purely random fluctuations. There is no trend or harmonic fluctuations. The power spectrum is uniformly distributed over all frequencies.

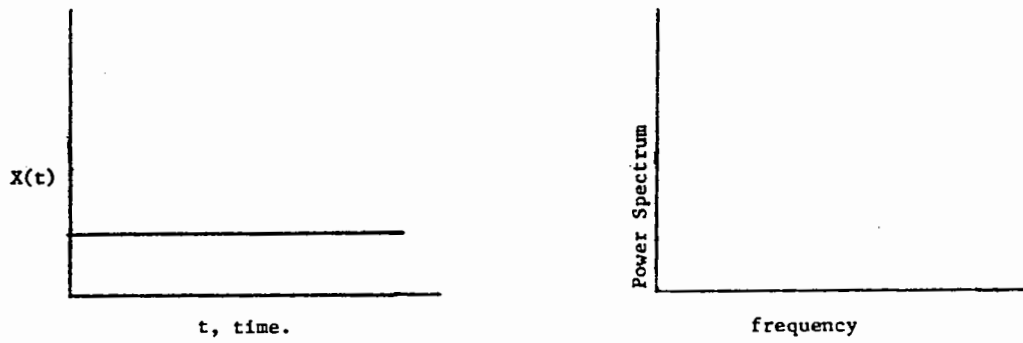
Figure 4.4e shows a record with purely random fluctuations superimposed on a linear trend. Its power spectrum is the superposition of power spectra corresponding to the linear trend record and the purely random record.

Figure 4.4f shows a record with purely random fluctuation superimposed on harmonic variations of frequency f_1 . Its power spectrum is the superposition of power spectra corresponding to the harmonic record and the purely random record.

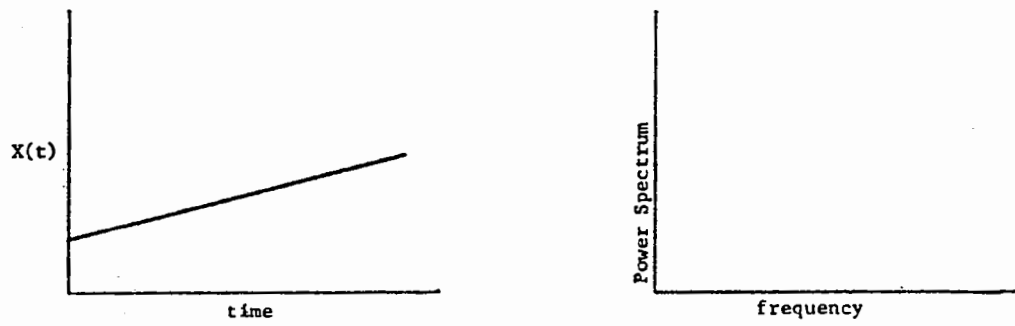
The power spectra depicted in Figure 4.4 are theoretical power spectra. They are based on infinite continuous records. In practice, records will be of finite duration and discrete. When evaluating the power spectrum of a finite duration record it is assumed that this finite record repeats itself periodically at intervals of length equal to the duration of the given record.

When dealing with discrete records or digital treatments of a continuous record, the frequency of data acquisition is a frequency foreign to the phenomenon under study which would appear in the power spectrum. These two practical limitations on spectral analysis lead to distortion in the low and high frequency regions of the spectrum known as "aliasing". The highest frequency which can be resolved from a discrete record with sampling interval Δt is the "Nyquist frequency"

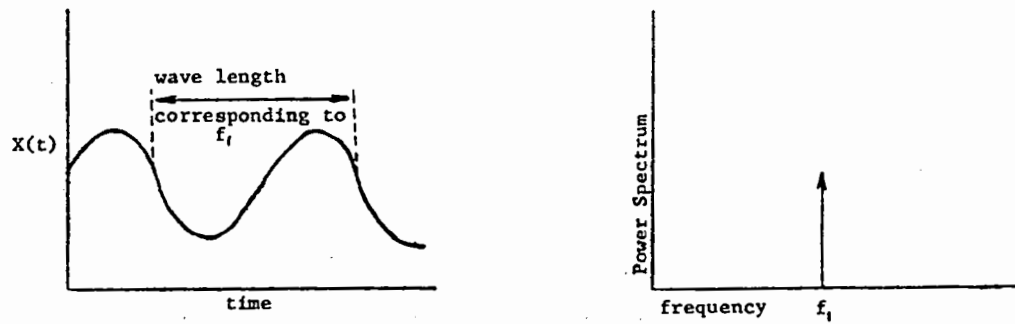
$$f_{\max} = \frac{1}{2 \Delta t}$$



(a) Constant record



(b) Linear trend record



(c) Harmonic record

Figure 4.4 Typical theoretical power spectra for several records

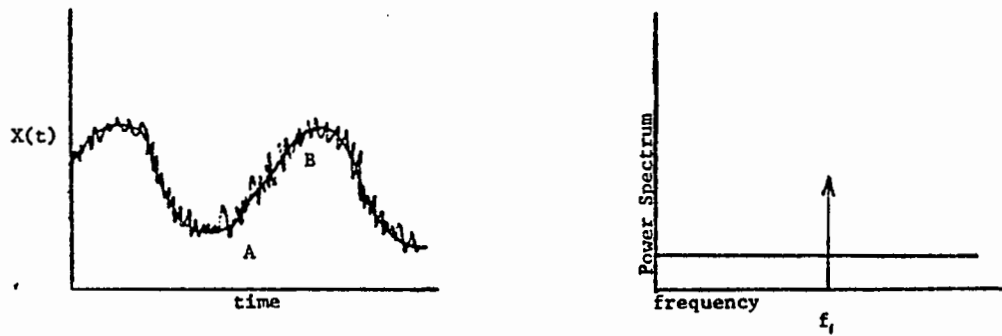
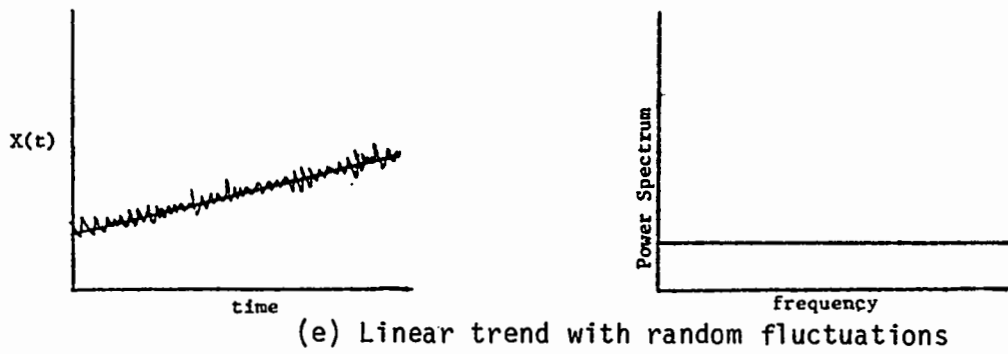
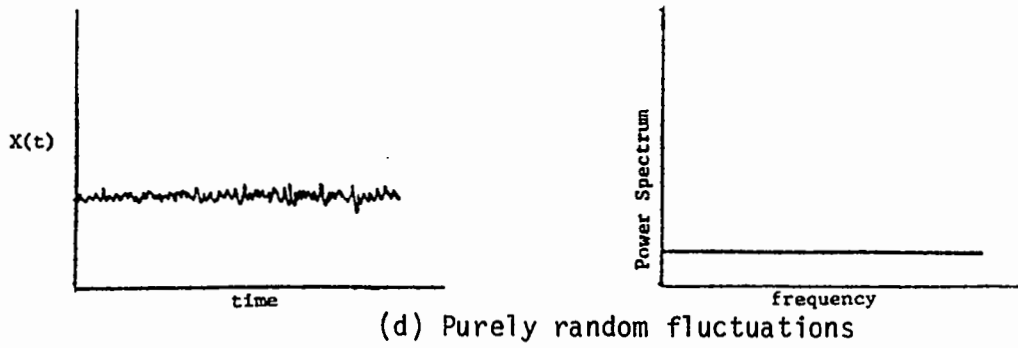


Figure 4.4 (Continued)

Furthermore, the length of the record should be large enough to resolve its periodic fluctuations. For example, spectral analysis of the portion AB of the record in Figure 4.4f would lead to a power spectrum similar to that of Figure 4.4e and not the actual power spectrum of Figure 4.4f.

Also, purely random fluctuations (white noise) are never met in practical applications where the theoretical power spectra depicted in Figures 4.4d-f would not be obtained. Rather, spectra similar to those of Figures 4.5a-c would be encountered. In Figure 4.5a the absence of any significant peak in the spectrum reflects the absence of any significant periodicity in the record of 4.4d. In Figure 4.5b the presence of a significant peak at the low frequency end of the spectrum is indicative of the linear trend in the record of Figure 4.4e. The significant peak at frequency f_1 on the spectrum of Figure 4.5c reflects the presence of the harmonic component of frequency f_1 in the record of Figure 4.4f.

The following rules of thumb should be followed when using spectral analysis:

- . The length of the record should be at least 10 times as long as the longest period of interest. For example, 10 years of data, if the annual period is the longest period of interest.
- . The sampling interval should be less than half the shortest period of interest, which would then have the Nyquist frequency. A sampling interval of one third or one fourth the length of the shortest period of interest is recommended.

In view of the length of record and the high frequency of data acquisition necessary for accurate spectral analysis, an overwhelming number of calculations will have to be carried out and treatment of the data on a digital computer is necessary. In carrying out spectral analysis with the aid of a digital computer, the practitioner may wish to write his own program or take advantage of existing programs such as BMD02T, BMD03T, BMD04T, or SPECTRA which are described in references (3)(4).

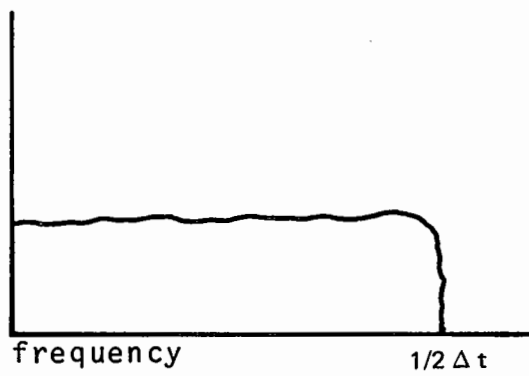
4.1.3 Probability Density Functions (1)(5)(6)

When data are not deterministic, that is when they cannot be defined by an explicit function, there may be a probability density function (pdf), denoted by $f_X(x)$, which describes the probabilistic properties using the formula:

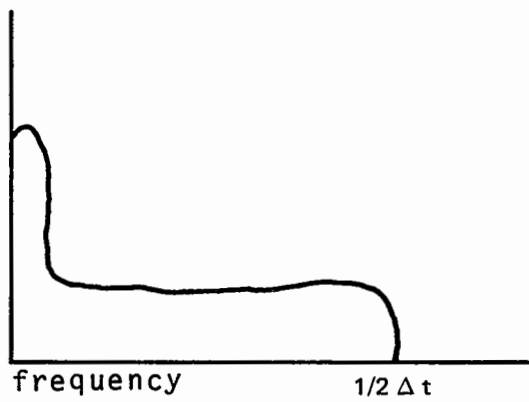
$$F_X(x) = P(X \leq x) = \int_{-\infty}^x f_X(u) du, \text{ for continuous functions, or}$$

$$F_X(x) = P(X \leq x) = u = \sum_{-\infty}^x f_X(u), \text{ for discrete functions}$$

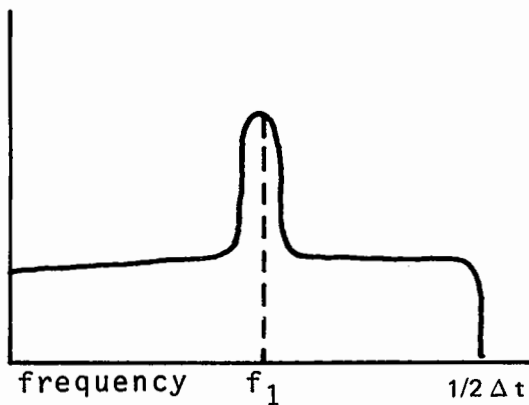
where $P(X \leq x)$ is read "the probability that X is less than or equal to a certain fixed value, x".



(a)



(b)



(c)

Figure 4.5 Typical practical power spectra for the records of Figure 4.4 d,e, and f

4.1.3.1 The Gaussian or Normal Distribution

This is a widely used and frequently found distribution because many natural occurrences tend to behave according to this distribution in the long run (sometimes very long). If X has a normal distribution with mean μ_x and variance σ_x^2 , then

$$f_X(x) = \frac{1}{\sigma_x \sqrt{2\pi}} \exp \left(-\frac{(x-\mu_x)^2}{2\sigma_x^2} \right) \text{ and so}$$

$$P(X \leq x) = \int_{-\infty}^x \frac{1}{\sigma_x \sqrt{2\pi}} \exp \left(-\frac{(t-\mu_x)^2}{2\sigma_x^2} \right) dt.$$

Using a substitution of $z = \frac{t-\mu_x}{\sigma_x}$ (and so $dz = \frac{dt}{\sigma_x}$), we get

$$P(X \leq x) = P\left(Z \leq \frac{x-\mu_x}{\sigma_x}\right) = \int_{-\infty}^{(x-\mu_x)/\sigma_x} \left(\frac{1}{\sqrt{2\pi}} \exp(-z^2/2) \right) dz.$$

It is easily seen that μ_x and σ_x define the function, so if it is known that data have a normal distribution and the mean and standard deviation are known, the probability distribution is completely defined. Another property of the normal distribution is that if X has a normal distribution with mean

μ_x and variance σ_x^2 [denoted $X \sim N(\mu_x, \sigma_x^2)$], $Z = \frac{X-\mu_x}{\sigma_x}$ has a normal

distribution with 0 mean and a variance of 1 (i.e. $Z \sim N(0,1)$) which is called the standard normal distribution.

Another property of the normal distribution is that randomly selected observations will have approximately a 68.3% probability of falling within the interval $\mu_x \pm \sigma_x$, 95.5% within the interval $\mu_x \pm 2\sigma_x$ and 99.7% within the interval $\mu_x \pm 3\sigma_x$. Figure 4.6 shows a graph of the normal distribution and illustrates this property.

4.1.3.2 The Pearson Type III Distribution

Unlike the normal distribution, which is defined from $-\infty$ to $+\infty$, this distribution is defined only on the range 0 to ∞ . The pdf of this distribution is given by

$$f_X(x) = \gamma_0 \exp(-\gamma x) \left(1 + \frac{\gamma x}{d}\right)^{\gamma d}$$

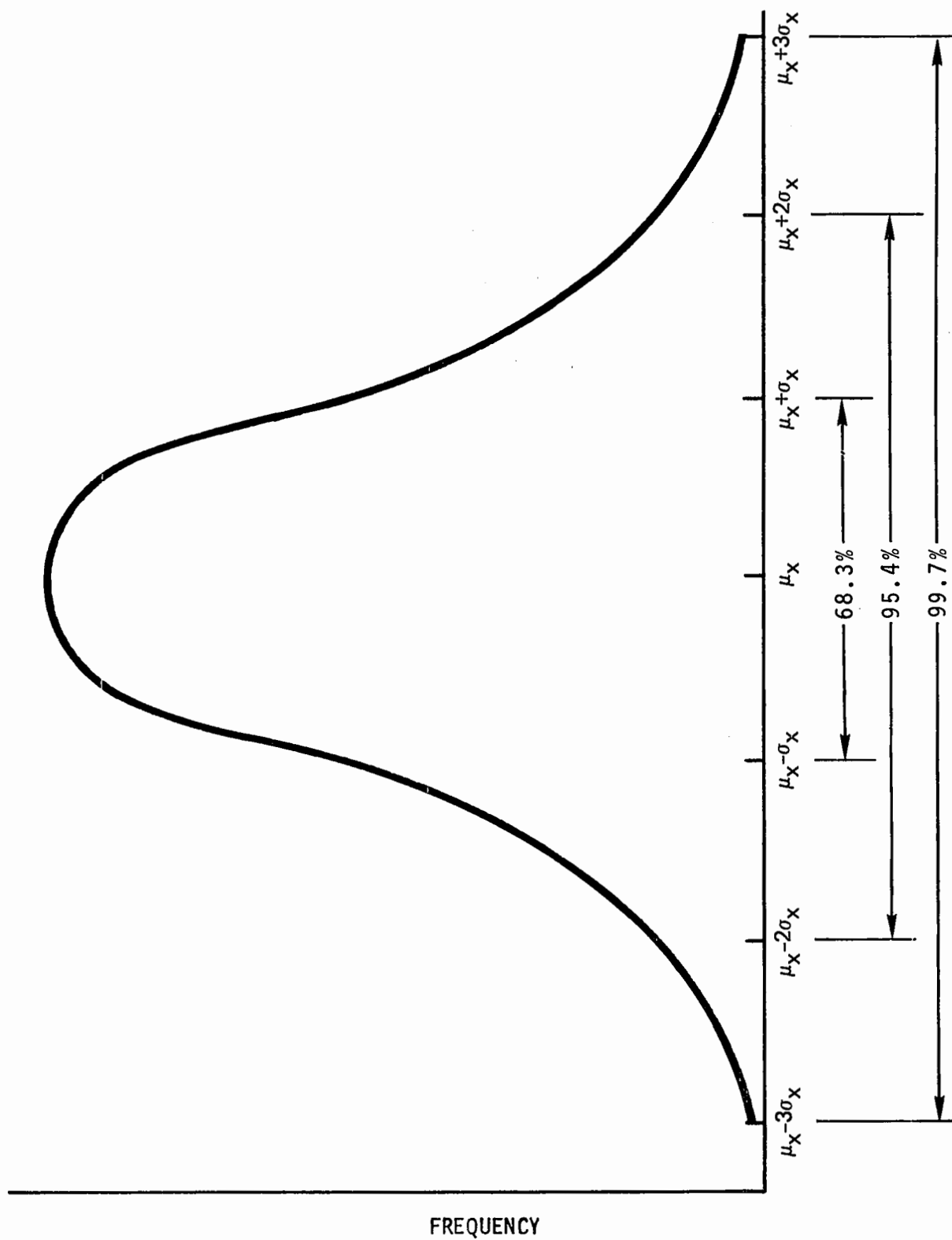


Figure 4.6 Gaussian or normal distribution

where γ_0 and γ are constants,

d is the distance between the mode (the value that occurs most often) and the origin.

4.1.3.3 Chi-Square Distribution

This is the probability distribution of a random variable of the form $X = Z_1^2 + Z_2^2 + \dots + Z_n^2$ where Z_1, \dots, Z_n are a set of n independent random variables each having a standard normal distribution and n is called the degrees of freedom of the distribution. The probability density function for a random variable X having a chi-square distribution with n degrees of freedom of the distribution. The probability density function for a random variable X having a chi-square distribution with n degrees of freedom

(denoted $X \sim \chi_n^2$) is given by

$$f_X(x) = \frac{1}{\Gamma(\frac{n}{2}) 2^{n/2}} x^{n/2-1} e^{-x/2} \quad \text{for } 0 < x < \infty$$

where $\Gamma(\alpha) = \int_0^\infty x^{\alpha-1} e^{-x} dx$.

It happens that n , the degrees of freedom, is the mean of the distribution (that is $n = \mu_X$) and the variance is $2n$ (or $2n = \sigma_X^2$).

4.1.3.4 Student's t - Distribution

A random variable X having a student's t - distribution (denoted $X \sim t_n$) with n degrees of freedom has a pdf of the form

$$f_X(x) = \frac{\Gamma((n+1)/2)}{\sqrt{\pi n} \Gamma(n/2)} \left[\frac{1}{(1 + x^2/n)^{(n+1)/2}} \right]$$

If $X \sim t_n$, then X can be expressed as the ratio $X = \frac{Z}{\sqrt{Y/n}}$

where $Z \sim N(0,1)$

$Y \sim \chi_n^2$ (Z and Y are independent random variables)

This shows the relationship between the t - distribution and the standard normal and chi-square distribution. It is also noteworthy that a student's t - distribution with infinite degrees of freedom is a standard normal distribution.

4.1.3.5 Determination of the Type of Distribution (5)

To apply the concepts of statistics, the type of distribution from which the observations came must be determined (or approximated). There are both graphical and numerical methods from accomplishing this.

Graphical Procedure for Small Sample ($N < 30$)

Step 1. Arrange the data in increasing order of magnitude as for finding the median, and assign a ranking number, m , to each value. The smallest observation will have rank 1 and largest will have rank N . (See column 1 of Table 4.7).

Step 2. Calculate the percent probability for each value, using the formula

$$P_m = \frac{50(2m-1)}{N} \text{ where } m \text{ is the rank as defined above and } P_m \text{ is}$$

the percent probability of an observation being less than or equal to the m^{th} value.

Step 3. Plot each value against its corresponding percent probability on the appropriate probability paper for the distribution of interest.

An example of data treatment is shown in Table 4.7 and Figure 4.7. If the data have a normal distribution, the plot will be a straight line on normal probability paper. If the data have a log-normal distribution, then they will yield a straight line when plotted on log probability paper. Notice that in this example the data approximate a straight line fairly well except near the upper end and at one point at the lower end. Even these do not show a large deviation from the straight line. This indicates that the data have an approximately normal distribution.

Using the facts that approximately 68.3% of the values are within the interval $\bar{X} \pm S_x$, and the percent probability of the mean of the normal distribution is 50 since the mean is equal to the median, S_x can be

graphically estimated from Figure 4.7. To do this, we find the interval on the horizontal axis, with the mean of 50 at its center and width 68.3, (making the end-points 15.85 and 84.15. Then, move up from the larger of these points to meet the line that approximates the distribution. Then, moving horizontally to the left, we read from the vertical axis the observation corresponding to this percent probability. The observation on the vertical axis corresponding to 50 on the horizontal axis, is also found, which, as was mentioned before, is the mean and also the median of the distribution, and could therefore be determined by finding the median of the data which are already arranged in increasing order. The difference between these two numbers is approximately equal to S_x , the standard deviation of

TABLE 4.7 COMPUTATIONAL TABLE FOR GRAPHICAL NORMAL OR PEARSON TYPE III
DISTRIBUTION DETERMINATION

Week (i)	Concentration (X_i)	Rank (m)	Plotting Position $p = \frac{50(2m-1)}{N}$
1	30.8	23	86.6
2	28.6	16	59.6
3	28.5	14	51.9
4	28.6	15	55.8
5	30.0	21	78.8
6	27.2	7	25.0
7	28.3	12	44.2
8	28.5	13	48.1
9	28.1	11	40.4
10	26.7	4	13.5
11	27.4	9	32.7
12	29.8	20	75.0
13	27.4	8	28.8
14	29.2	17	63.5
15	26.1	3	9.6
16	25.9	1	1.9
17	27.9	10	36.5
18	32.4	25	94.2
19	27.0	6	21.2
20	26.8	5	17.3
21	30.6	22	82.7
22	34.6	26	98.1
23	29.6	19	71.2
24	26.0	2	5.8
25	31.5	24	90.4
26	29.5	18	67.3

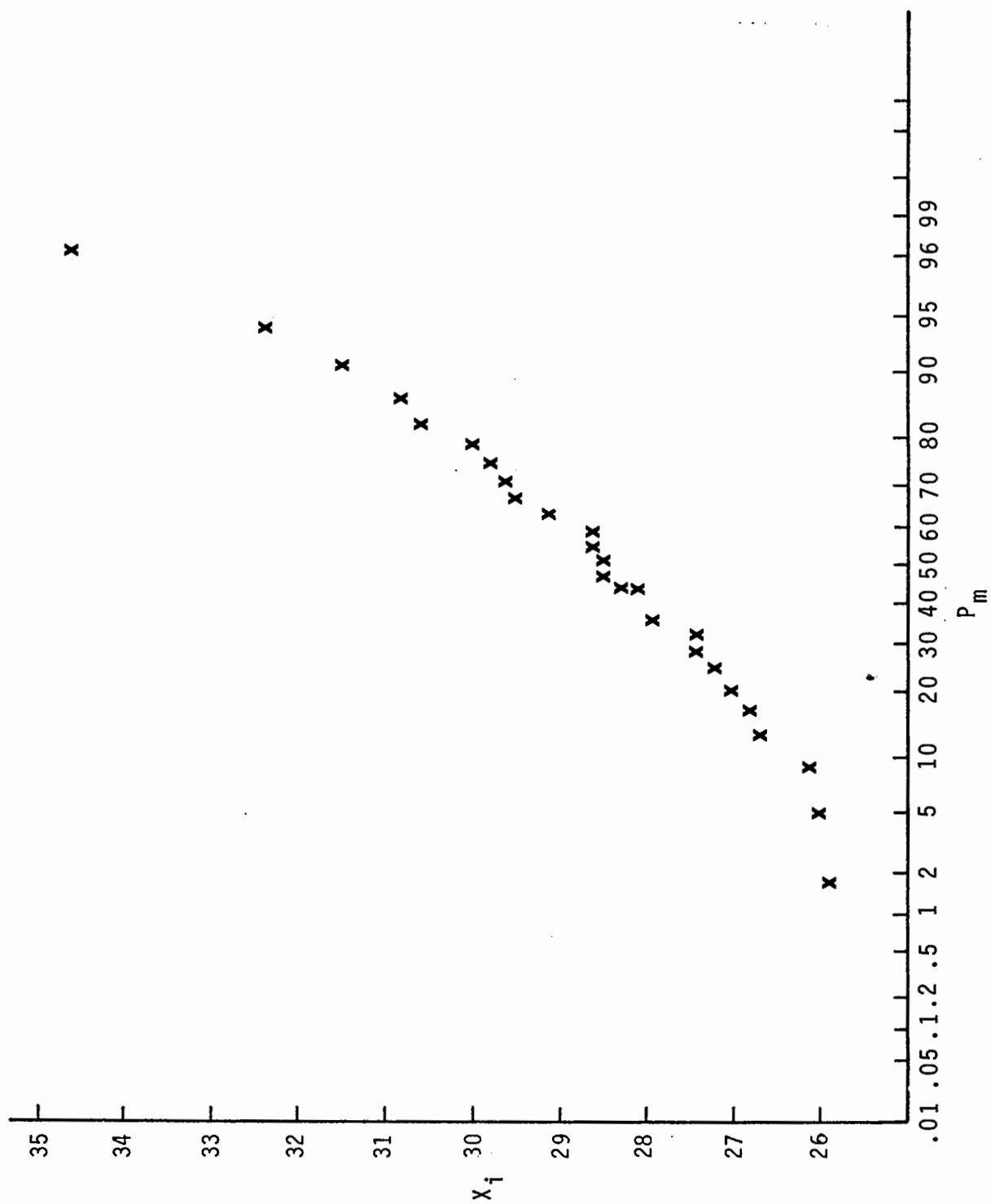


Figure 4.7 P_m vs X_i plot for data in Table 4.7

the data. (Note that the more the plotted points deviate from a straight line, the less accurate this estimate will be). Figure 4.8 shows the data have an approximate normal distribution with mean 28.7 and standard deviation $(30.8 - 26.6)/2 = 2.1$.

Computational Method (8)

Another method for estimating the distribution of a data set uses the coefficient of skewness, along with the mean and standard deviation, all of which were defined earlier. The following has been recommended as a relationship between the coefficient of skewness and the best approximating probability distribution:

<u>Coefficient of Skewness, (k)</u>	<u>Best Fitting Probability Distribution</u>
< 0.5	Normal
0.9 - 1.6	Pearson Type III
> 1.7	Log-Normal

Since these ranges of skewness were empirically determined and it is impractical to have gaps between the ranges, it seems reasonable to interpolate and thus end up with the following adjusted table:

<u>Coefficient of Skewness, (k)</u>	<u>Best Fitting Probability Distribution</u>
< 0.7	Normal
0.7 - 1.7	Pearson Type III
> 1.7	Log-Normal

Using the data from Table 4.1 compute the coefficient of skewness using

$$k = \frac{N \sum_{i=1}^N (X_i - \bar{X})^3}{(N-1)(N-2) S_x^3}$$

which was found in Section 4.1.1. to be 0.63. As recommended above assume that these data have a normal distribution with mean 33.6 and standard deviation 2.07 (that is, $X \sim N(33.6, 4.28)$).

Admittedly, this is a rather informal way of selecting an assumption for the underlying distribution. If more rigorous justification is required to support the distribution assumption, please consult a qualified statistician for more formal techniques.

4.1.3.6 Normal Tables (Table 4.8)

Statistics texts and books of mathematical tables usually contain a table which gives the area under the standard normal curve to the right of a given value z , which is $P\{X > z\}$ ($= P\{X < -z\}$), so that one need not evaluate the

integral $\int_z^{+\infty} f_X(t)dt$, to find the probabilities. Appendix B briefly discusses the relation between the integral and Table 4.8.

Example 1:

Find $P\{X < -1.93\}$ if $X \sim N(0,1)$

This probability is equivalent to $P\{X > 1.93\} = 0.0268$ from Table 4.8.

Example 2:

Find the number z such that $P\{X > z\} = .14345$. Looking in the body of the table, it is necessary to interpolate between 1.06 and 1.07 to find z , since .14345 is halfway between 0.1423 and 0.1446.

$$z = \frac{1.06 + 1.07}{2} = 1.065$$

4.1.4 Hypothesis Testing(1)(5)

A common use of statistics is in testing whether a sample came from a particular distribution with specific parameters. It is known that if X has a normal distribution with mean μ_X and variance σ_X^2 , then

$$Z = \frac{X - \mu_X}{\sigma_X} \quad \text{has a standard normal distribution. A theorem}$$

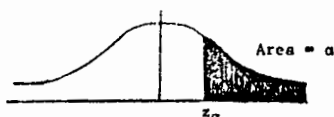
in statistics states that for a large sample (usually $N > 30$) from any distribution, \bar{X} will have an approximately normal distribution with mean $\mu_{\bar{X}} = \mu_X$ and variance $\sigma_{\bar{X}}^2 = \sigma_X^2/N$. Using this information, the hypotheses about μ_X can be tested.

Example:

Choose a random sample of 100 observations from a population with $\mu_X = 300$ and $\sigma_X = 70$. Find the probability that \bar{X} , the sample mean, is 286 or less. Assume that \bar{X} is normally distributed, and so

TABLE 4.8 AREAS UNDER STANDARDIZED NORMAL DENSITY FUNCTION (9)

$$\text{Value of } \alpha = \int_{z_\alpha}^{\infty} \frac{1}{\sqrt{2\pi}} \exp(-z^2/2) - P(z > z_\alpha)$$



z_α	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	0.5000	0.4960	0.4920	0.4880	0.4840	0.4801	0.4761	0.4721	0.4681	0.4641
0.1	0.4602	0.4562	0.4522	0.4483	0.4443	0.4404	0.4364	0.4325	0.4268	0.4247
0.2	0.4207	0.4168	0.4129	0.4090	0.4052	0.4013	0.3974	0.3936	0.3897	0.3859
0.3	0.3821	0.3783	0.3745	0.3707	0.3669	0.3632	0.3594	0.3557	0.3520	0.3483
0.4	0.3446	0.3409	0.3372	0.3336	0.3300	0.3264	0.3228	0.3192	0.3156	0.3121
0.5	0.3085	0.3050	0.3015	0.2981	0.2946	0.2912	0.2877	0.2843	0.2810	0.2776
0.6	0.2743	0.2709	0.2676	0.2643	0.2611	0.2578	0.2546	0.2514	0.2483	0.2451
0.7	0.2420	0.2389	0.2358	0.2327	0.2296	0.2266	0.2236	0.2206	0.2177	0.2148
0.8	0.2119	0.2090	0.2061	0.2033	0.2005	0.1977	0.1949	0.1922	0.1894	0.1867
0.9	0.1841	0.1814	0.1788	0.1762	0.1736	0.1711	0.1685	0.1660	0.1635	0.1611
1.0	0.1587	0.1562	0.1539	0.1515	0.1492	0.1469	0.1446	0.1423	0.1401	0.1379
1.1	0.1357	0.1335	0.1314	0.1292	0.1271	0.1251	0.1230	0.1210	0.1190	0.1170
1.2	0.1151	0.1131	0.1112	0.1093	0.1075	0.1056	0.1038	0.1020	0.1003	0.0985
1.3	0.0968	0.0951	0.0934	0.0918	0.0901	0.0885	0.0869	0.0853	0.0838	0.0823
1.4	0.0808	0.0793	0.0778	0.0764	0.0749	0.0735	0.0721	0.0708	0.0694	0.0681
1.5	0.0668	0.0665	0.0643	0.0630	0.0618	0.0606	0.0594	0.0582	0.0571	0.0559
1.6	0.0584	0.0537	0.0526	0.0516	0.0505	0.0495	0.0485	0.0475	0.0465	0.0455
1.7	0.0446	0.0436	0.0427	0.0418	0.0409	0.0401	0.0392	0.0384	0.0375	0.0367
1.8	0.0359	0.0351	0.0344	0.0336	0.0329	0.0322	0.0314	0.0307	0.0301	0.0294
1.9	0.0287	0.0281	0.0274	0.0268	0.0262	0.0256	0.0250	0.0244	0.0239	0.0233
2.0	0.0228	0.0222	0.0217	0.0212	0.0207	0.0202	0.0197	0.0192	0.0188	0.0183
2.1	0.0179	0.0174	0.0170	0.0166	0.0162	0.0158	0.0154	0.0150	0.0146	0.0143
2.2	0.0139	0.0136	0.0132	0.0129	0.0125	0.0122	0.0119	0.0116	0.0113	0.0110
2.3	0.0107	0.0104	0.0102	0.00990	0.00964	0.00939	0.00914	0.00889	0.00866	0.00842
2.4	0.00820	0.00798	0.00776	0.00755	0.00734	0.00714	0.00695	0.00676	0.00657	0.00639
2.5	0.00621	0.00604	0.00587	0.00570	0.00554	0.00539	0.00523	0.00508	0.00494	0.00480
2.6	0.00466	0.00453	0.00440	0.00427	0.00415	0.00402	0.00391	0.00379	0.00368	0.00357
2.7	0.00347	0.00336	0.00326	0.00317	0.00307	0.00298	0.00289	0.00280	0.00272	0.00264
2.8	0.00256	0.00248	0.00240	0.00233	0.00226	0.00219	0.00212	0.00205	0.00199	0.00193
9	0.00187	0.00181	0.00175	0.00169	0.00164	0.00159	0.00154	0.00149	0.00144	0.00139

$$Z = \frac{X - u_{\bar{X}}}{\sigma_{\bar{X}}} = \frac{X - \mu_X}{\sigma_X / \sqrt{N}} \quad \text{has a standard normal}$$

distribution. In this example, $Z = \frac{286-300}{70/\sqrt{100}} = -2$

Turning to a table of areas under the standard normal curve (Table 4.8), the area to the left of -2, which is the same as the area to the right of 2, is 0.0228, which is, then, the probability that X is less than or equal to 286 and is written $P(X \leq 286) = 0.0228$. This means that if a larger number of samples of size 100 are taken from this population, approximately 2.3% of them will have sample means of 286 or less.

If the population parameters (μ_X and σ_X^2) are unknown, this method can be used to make inferences about them. Suppose it is known that $\sigma_X = 70$ and that the mean of a random sample (X) with $N = 100$ is 318. Can it be reasonably assumed that the population mean, μ_X is 300?

Test to see if $\mu_X = 300$. This hypothesized value is called μ_0 and the hypothesis that $\mu_X = \mu_0$ is called H_0 (the null hypothesis). Write the null

hypothesis: $H_0 : \mu_X = \mu_0$ (in this case, $H_0 : \mu_X = 300$)

The alternative is that $\mu_X \neq 300$. This is called the alternative hypothesis and is denoted $H_1 : \mu_X \neq \mu_0$. $Z_{\alpha/2} = Z_{.025} = 1.96$ and so the critical region for the rejection of H_0 is $\{z; z \leq -1.96 \text{ or } z \geq 1.96\}$.

The test statistic used is

$$z = \frac{\bar{X} - u_0}{\sigma_{\bar{X}}} = \frac{318-300}{70/\sqrt{100}} = 2.57$$

In this case $z = 2.57 > 1.96 = Z_{\alpha/2}$, and so reject H_0 and conclude that the distribution from which the sample was taken has a mean other than 300.

If both u_X and σ_X are unknown, the z-statistic as above cannot be used, since its calculation involves σ_X , so use the statistic

$$t = \frac{\bar{X} - u_0}{S_X / \sqrt{N}} \quad \text{which has a Student's t-distribution.}$$

Example:

If in the above example, the standard deviation is unknown, but the sample standard deviation is found to be 70.5, then the test statistic is

$$t = \frac{318-300}{70.5/\sqrt{100}} = 2.55.$$

Using Table 4.9 which gives values of $t_{n;\alpha}$ (which is the number such that

$P(t_n > t_{n;\alpha}) = \alpha$, where t_n has a Student's t-distribution with n degrees of freedom), look under $\alpha = .025$ (since a two-tailed test at the .05 level of significance is being used) and $n=99$. (The degrees of freedom, n , is just $N-1$). Since $n=99$ does not appear in the table, take the number approximately 2/3 of the way between $n=60$ and $n=120$. The test statistic, $t=2.55$, is greater than that for $n=60$, and so reject $H_0 : \mu_x = 300$ in favor of $H_1 : \mu_x \neq 300$.

Example:

If a different sample is taken, say of size 121, from the same population and a sample mean of 310 and a sample standard deviation 70.2 are computed, the following results:

$$t = \frac{\bar{x} - \mu_0}{s_x/\sqrt{N}} = \frac{310-300}{70.2/\sqrt{121}} = 1.56.$$

Looking in Table 4.9 for $\alpha = .025$ and $n = N - 1 = 120$, it is discovered that $t_{120;.025} = 1.980$, and so the test statistic does not fall in the critical region. Therefore, H_0 cannot be rejected.

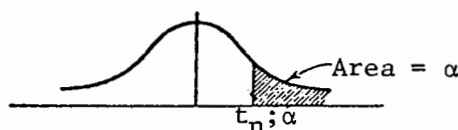
4.1.5 Confidence Intervals

4.1.5.1 Confidence Intervals for the Mean (1)(5)

In the example above, a hypothesis about the population mean was tested. In a similar way, an interval could be constructed within which would be considered a hypothesis for the mean tenable and outside of which such a hypothesis would be untenable. This interval is called a confidence interval and its end-points confidence limits.

In the previous example, a population mean of 300 was found to be consistent with the computed statistics. Suppose $H_0: \mu_x = 295$ was tested against $H_1: \mu_x \neq 295$. Then

$$t = \frac{\bar{x} - \mu_0}{s_x/\sqrt{N}} = 2.35 \quad \text{which is greater than}$$

TABLE 4.9 PERCENTAGE POINTS OF STUDENT t -DISTRIBUTION (9)Value of $t_{n;\alpha}$ such that $P(t > t_{n;\alpha}) = \alpha$ 

n	α				
	0.10	0.050	0.025	0.010	0.005
1	3.078	6.314	12.706	31.821	63.657
2	1.886	2.920	4.303	6.965	9.925
3	1.638	2.353	3.182	4.541	5.841
4	1.533	2.132	2.776	3.747	4.604
5	1.476	2.015	2.571	3.365	4.032
6	1.440	1.943	2.447	3.143	3.707
7	1.415	1.895	2.365	2.998	3.499
8	1.397	1.860	2.306	2.896	3.355
9	1.383	1.833	2.262	2.821	3.250
10	1.372	1.812	2.228	2.764	3.169
11	1.363	1.796	2.201	2.718	3.106
12	1.356	1.782	2.179	2.681	3.055
13	1.350	1.771	2.160	2.650	3.012
14	1.345	1.761	2.145	2.624	2.977
15	1.341	1.753	2.131	2.602	2.947
16	1.337	1.746	2.120	2.583	2.921
17	1.333	1.740	2.110	2.567	2.898
18	1.330	1.734	2.101	2.552	2.878
19	1.328	1.729	2.093	2.539	2.861
20	1.325	1.725	2.086	2.528	2.845
21	1.323	1.721	2.080	2.518	2.831
22	1.321	1.717	2.074	2.508	2.819
23	1.319	1.714	2.069	2.500	2.807
24	1.318	1.711	2.064	2.492	2.797
25	1.316	1.708	2.060	2.485	2.787
26	1.315	1.706	2.056	2.479	2.779
27	1.314	1.703	2.052	2.473	2.771
28	1.313	1.701	2.048	2.467	2.763
29	1.311	1.699	2.045	2.462	2.756
30	1.310	1.697	2.042	2.457	2.750
40	1.303	1.684	2.021	2.423	2.704
60	1.296	1.671	2.000	2.390	2.660
120	1.289	1.658	1.980	2.358	2.617

$\alpha = 0.995, 0.990, 0.975, 0.950$, and 0.900 follow from $t_{n;1-\alpha} = -t_{n;\alpha}$

$t_{120;.025} = 1.980$, so reject H_0 in favor of H_1 . Somewhere between 295 and 300 is a mean such that the computed t is equal to $t_{n; \alpha}$, and this number is the lower confidence limit for the population mean. Similarly, if $H_0: \mu_x = 322$ is tested against $H_1: \mu_x \neq 322$, $t = -1.88$, which is greater than $-t_{120;.025}$, and so H_0 is acceptable. But a test of $H_0: \mu_x = 323$ yields $t = -2.03 < -1.98$ and so H_0 is rejected. Therefore, the upper confidence limit is between 322 and 323. The actual confidence limits for μ_x can be computed from

$$t_{N-1; \alpha/2} = \frac{\bar{x} - \bar{\mu}_x}{S_x / \sqrt{N}} \text{ and } -t_{N-1; \alpha/2} = \frac{\bar{x} - \bar{\mu}_x}{S_x / \sqrt{N}}$$

which in this example yield:

$$\mu_L = -(t_{120;.025} \cdot \frac{S_x}{\sqrt{N}} - \bar{x}) = (-1.98 \cdot \frac{70.2}{\sqrt{121}} - 310) = 297.4$$

$$\text{and: } \mu_U = -(-1.98 \cdot \frac{70.2}{\sqrt{121}} - 310) = 322.6$$

Since $\alpha = 0.05$ (and $1 - \alpha = .95$), 95% of all intervals constructed in this way will contain the population mean μ_x , and so are called 95% confidence intervals or limits for μ_x . (If $\alpha = .01$, we construct a 99% confidence

interval). Without going through the above derivation, the confidence limits can be computed using the following formulas:

$$\mu_U = \bar{x} + \frac{S_x}{\sqrt{N}} (t_{N-1; \alpha/2})$$

$$\mu_L = \bar{x} - \frac{S_x}{\sqrt{N}} (t_{N-1; \alpha/2})$$

4.1.5.2 Confidence Interval for the Variance

4.1.5.2.1 Confidence Interval for σ_x^2 if μ_x is known

If X has a normal distribution, then

$\frac{X - \mu_X}{\sigma_X}$ has a standard normal distribution.

If X_1, X_2, \dots, X_N all have a normal distribution with the same mean μ and the same variance σ^2 , then

$$Y = \sum_{i=1}^N \frac{(X_i - \mu)^2}{\sigma^2} \quad \text{has a } \chi_n^2 \text{ distribution (i.e. a chi-square}$$

distribution with n degrees of freedom).

Using a chi-square table (Table 4.10), construct a 95% confidence interval for σ^2 as follows:

Find: $\chi_{N; \alpha/2}^2$, which is the number that:

$$P(Y < \chi_{N; \alpha/2}^2) = \alpha/2 = .025, \text{ for } \alpha = .05$$

Also find: $\chi_{N; 1 - \alpha/2}^2 = \chi_{N; .975}^2$

Now $P(\chi_{N; \alpha/2}^2 < Y < \chi_{N; 1 - \alpha/2}^2) = .975 - .025 = .95$, and so the numbers

$\chi_{N; \alpha/2}^2$ and $\chi_{N; 1 - \alpha/2}^2$ are 95% confidence limits for Y .

Since:

$$Y = \sum_{i=1}^N \frac{(X_i - \mu)^2}{\sigma^2}, \quad P(\chi_{N; .025}^2 < \sum_{i=1}^N \frac{(X_i - \mu)^2}{\sigma^2} < \chi_{N; .975}^2) = .95,$$

which can be written as:

$$P\left[\frac{1}{\chi_{N; .025}^2} \sum_{i=1}^N (X_i - \mu)^2 > \sigma^2 > \frac{1}{\chi_{N; .975}^2} \sum_{i=1}^N (X_i - \mu)^2\right] = .95$$

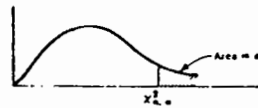
and so a 95% confidence interval for σ^2 is obtained.

Example:

Suppose there are 10 observations from a normal distribution with mean 0 (i.e. $N = 10, \mu_X = 0$). Then $(X_i - \mu_X)^2 = (X_i - 0)^2 = X_i^2$ and so:

TABLE 4.10 PERCENTAGE POINTS OF CHI-SQUARE DISTRIBUTION
(9)

Value of $\chi^2_{n,\alpha}$ such that $\text{Prob}(\chi^2_n > \chi^2_{n,\alpha}) = \alpha$



n	α									
	0.995	0.990	0.975	0.950	0.900	0.10	0.05	0.025	0.010	0.005
1	0.000039	0.00016	0.00098	0.0039	0.0158	2.71	3.84	5.02	6.63	7.88
2	0.0100	0.0201	0.0506	0.103	0.211	4.61	5.99	7.38	9.21	10.60
3	0.0717	0.115	0.216	0.352	0.584	6.25	7.81	9.35	11.34	12.84
4	0.207	0.297	0.484	0.711	1.06	7.78	9.49	11.14	13.28	14.86
5	0.412	0.554	0.831	1.15	1.61	9.24	11.07	12.83	15.09	16.75
6	0.676	0.872	1.24	1.64	2.20	10.64	12.59	14.45	16.81	18.55
7	0.989	1.24	1.69	2.17	2.83	12.02	14.07	16.01	18.48	20.28
8	1.34	1.65	2.18	2.73	3.49	13.36	15.51	17.53	20.09	21.96
9	1.73	2.09	2.70	3.33	4.17	14.68	16.92	19.02	21.67	23.59
10	2.16	2.56	3.25	3.94	4.87	15.99	18.31	20.48	23.21	25.19
11	2.60	3.05	3.82	4.57	5.58	17.28	19.68	21.92	24.73	26.76
12	3.07	3.57	4.40	5.23	6.30	18.55	21.03	23.34	26.22	28.30
13	3.57	4.11	5.01	5.89	7.04	19.81	22.36	24.74	27.69	29.82
14	4.07	4.66	5.63	6.57	7.79	21.06	23.68	26.12	29.14	31.32
15	4.60	5.23	6.26	7.26	8.55	22.31	25.00	27.49	30.58	32.80
16	5.14	5.81	6.91	7.96	9.31	23.54	26.30	28.85	32.00	34.27
17	5.70	6.41	7.56	8.67	10.08	24.77	27.59	30.19	33.41	35.72
18	6.26	7.01	8.23	9.39	10.86	25.99	28.87	31.53	34.81	37.16
19	6.84	7.63	8.91	10.12	11.65	27.20	30.14	32.85	36.19	38.58
20	7.43	8.26	9.59	10.85	12.44	28.41	31.41	34.17	37.57	40.00
21	8.03	8.90	10.28	11.59	13.24	29.62	32.67	35.48	38.93	41.40
22	8.64	9.54	10.98	12.34	14.04	30.81	33.92	36.78	40.29	42.80
23	9.26	10.20	11.69	13.09	14.85	32.01	35.17	38.08	41.64	44.18
24	9.89	10.86	12.40	13.85	15.66	33.20	36.42	39.36	42.98	45.56
25	10.52	11.52	13.12	14.61	16.47	34.38	37.65	40.65	44.31	46.93
26	11.16	12.20	13.84	15.38	17.29	35.56	38.88	41.92	45.64	48.29
27	11.81	12.88	14.57	16.15	18.11	36.74	40.11	43.19	46.96	49.64
28	12.46	13.56	15.31	16.93	18.94	37.92	41.34	44.46	48.28	50.99
29	13.12	14.26	16.05	17.71	19.77	39.09	42.56	45.72	49.59	52.34
30	13.79	14.95	16.79	18.49	20.60	40.26	43.77	46.98	50.89	53.67
40	20.71	22.16	24.43	26.51	29.05	51.81	55.76	59.34	63.69	66.77
60	35.53	37.48	40.48	43.19	46.46	74.40	79.08	83.30	88.38	91.95
120	83.85	86.92	91.58	95.70	100.62	140.23	146.57	152.21	158.95	163.65

For $n > 120$, $\chi^2_{n,\alpha} \approx n \left[1 - \frac{2}{9n} + z_{\alpha} \sqrt{\frac{2}{9n}} \right]^3$ where z_{α} is the desired percentage point for a standardized normal distribution.

$$\sum_{i=1}^{10} (X_i - u_x)^2 = \sum_{i=1}^{10} X_i^2. \text{ Let this sum be equal to 113.45.}$$

A 95% confidence interval ($\alpha/2 = .025$) for σ^2 is then:

$$\left[\frac{113.45}{20.48}, \frac{113.45}{3.25} \right] = (5.5, 34.9).$$

4.1.5.2.2 Confidence Interval for σ_x^2 if μ_x is Unknown

It is also true (by the definition of S_x^2) that

$$\frac{(N-1)S_x^2}{\sigma_x^2}$$

has a chi-square distribution with $N-1$ degrees of freedom (χ_{N-1}^2) and so if μ_x is unknown, a confidence interval can be found using S_x^2 , the sample variance. Suppose in the above example, $S_x = 3.6$. Turn to Table 4.10 again and find $\chi_{9;.025}^2$ and $\chi_{9;.975}^2$, which are 19.02 and 2.70, and so the interval is:

$$\frac{NS_x^2}{\chi_{9;.975}^2}, \frac{NS_x^2}{\chi_{9;.025}^2} = \frac{9 \times 12.96}{2.70}, \frac{9 \times 12.96}{19.02} = (6.1, 43.2)$$

The confidence limits for the standard deviation are found by taking the square root of those for the variance.

4.1.5.3 Relative Error of the Standard Deviation

$$\frac{\Omega}{S_x} = \sqrt{N} \left[(\chi_{N-1; 1-\alpha/2}^2)^{-\frac{1}{2}} - (\chi_{N-1; \alpha/2}^2)^{-\frac{1}{2}} \right]$$

where Ω is the width of the confidence interval of the standard deviation

$$\chi_{N-1; 1-\alpha/2}^2 \text{ is defined above}$$

$(1-\alpha) \times 100\%$ is the level of confidence of the interval.

4.2 DETERMINATION OF NUMBER OF SAMPLES (10)

The number of samples necessary to reasonably characterize a water or wastewater is determined after collecting some background data on the concentration and variance of the concentration of the parameters under consideration. These values can be estimated; however, estimation will decrease the confidence in the results. Two techniques can be used to calculate the number of samples, one based on the allowed sample variability, the other on the accuracy of the sample mean. Each will give a desired value of N , the number of samples needed, with the larger value to be chosen for application.

4.2.1 Determining Number of Samples from a Constraint on the Variability

To apply this method, the following information is needed:

1. Allowable error of the standard deviation $\frac{\Omega}{S_x}$
2. Confidence level required $(1-\alpha)$

Therefore, for this situation, one is estimating that the value of a certain variable will occur within a specific interval. A normal distribution of the data is assumed. The data should be checked for normality as in Section 4.1.3.1.

Example:

Determine the number of samples required from a wastewater monitoring program such that the estimated standard deviation will be within 25% of its true value (i.e. $\pm 12.5\%$) at a confidence level of 98%.

Here $\alpha = 1 - .98 = .02$ and $\frac{\Omega}{S_x} = 0.25$. From Figure 4.8, the value of $\frac{\Omega}{S_x} = 0.25$ is found on the vertical axis and a horizontal line is followed until the curve for $\alpha = .02$ is met. Then a vertical line is dropped to the horizontal axis to find the number of observations needed ($N = 180$ in this case).

4.2.2 Determining Number of Samples from a Constraint on the Mean Value

To apply this method, the following information is required:

1. Confidence level required $(1-\alpha)$
2. Coefficient of variation of the source to be sampled $(CV = \frac{S_x}{\bar{X}})$
3. The required accuracy of the sample mean

A double iteration procedure is recommended, especially if the number of samples is found to be small ($N < 30$). For this calculation a normal distribution is assumed.

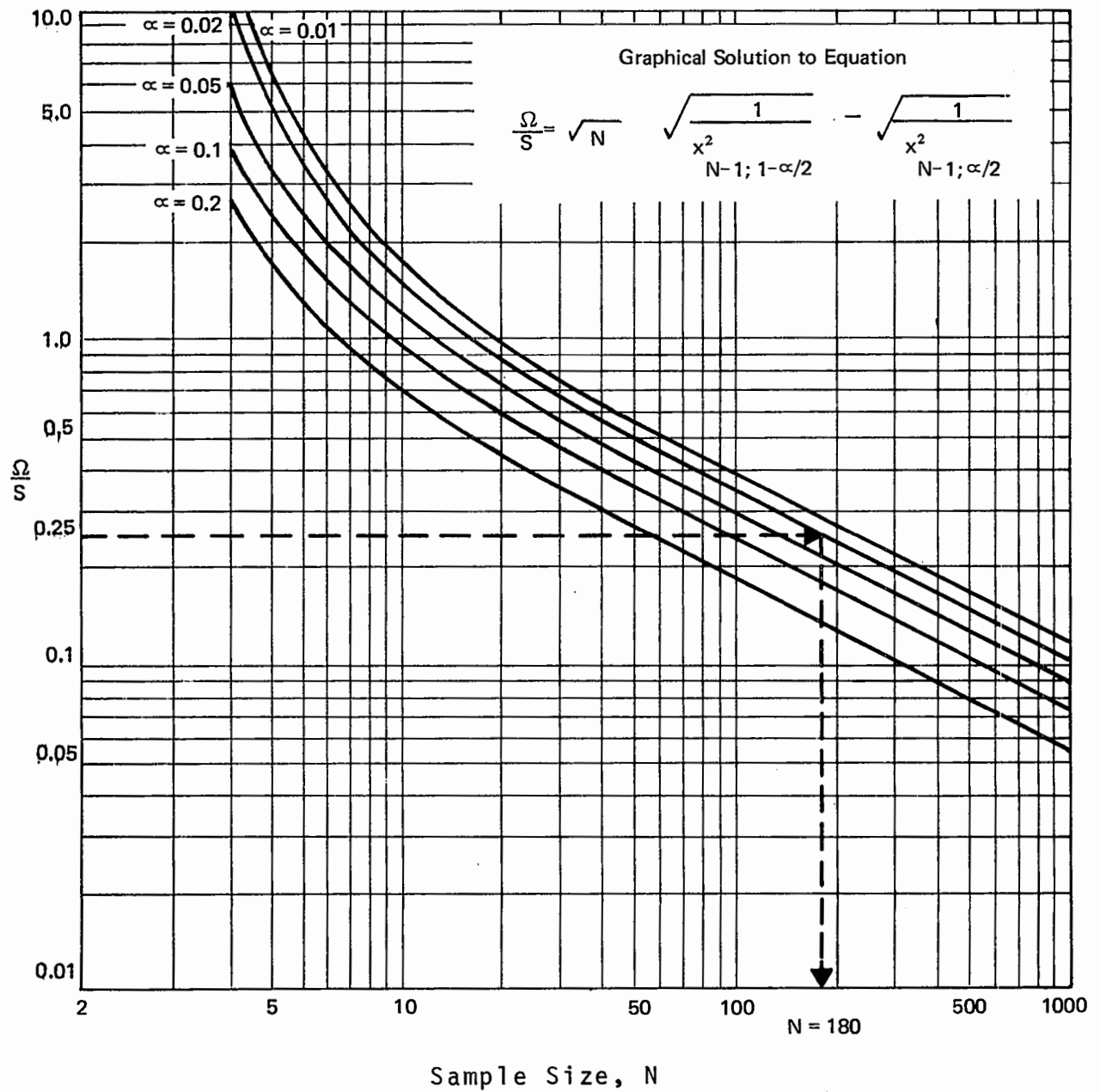


Figure 4.8 Determination of the number of samples based on the required accuracy of extreme values

The first iteration uses the formula:
$$N' = \left(\frac{CV \times Z_{\alpha/2}}{D/100} \right)^2$$

where:

D is the allowed deviation of the sample mean from the true mean, expressed as a percent of the true mean.

$Z_{\alpha/2}$ is found in Table 4.8.

For the second iteration, use:
$$N = \left(\frac{CV \times t_{\alpha/2; N'-1}}{D/100} \right)^2$$

where $t_{\alpha/2; N'-1}$ is found in Table 4.9.

Example:

For a wastewater stream with an average daily concentration of 120 mg/l BOD and a standard deviation of 32 mg/l, determine the number of daily samples which would provide an accuracy of the daily averages within 5%.

$$D = 5$$

$$\bar{X} = 120$$

$$S_x = 32$$

$$CV = \frac{S_x}{\bar{X}} = \frac{32}{120} = 0.27$$

If $\alpha = .05$ (95% confidence level) is chosen, then $Z_{\alpha/2} = Z_{.025}$ is found in Table 4.8 to be 1.96.

$$\text{Step 1} \quad N' = \left(\frac{0.27 \times 1.962}{5/100} \right)^2 = 109.3 = 110 \text{ samples}$$

Step 2 Using $N' = 110$, find $t_{\alpha/2; N'-1} = t_{.025; 109}$ in Table 4.9 to

be approximately 1.983 (using linear interpolation), so

$$N = \left(\frac{0.27 \times 1.983}{5/100} \right)^2 = 114.6 = 115 \text{ samples}$$

If the accuracies of both the standard deviation and the mean are used as criteria, choose the larger of the two values of N. In the example above, $N = 180$ from the constraint on S, and $N = 115$ from the constraint on \bar{X} , so 180 daily samples should be taken.

4.3 DETERMINING SAMPLE FREQUENCY

Although it requires the use of a digital computer, spectral analysis is the method that should be used for determining sampling frequency because of its accuracy and the simplicity of the final interpretation.

4.3.1 Determination of the Sampling Frequency from Power Spectra (11)(12) (13)(14)

It is imperative that a good set of historical data be available for analysis. Ideally, these data should be a continuous record of the characteristics being studied. Practically, they should be taken at a frequency that is higher than the highest expected frequency of harmonic variation components of the record. For example, if daily trends are to be analyzed, hourly samples may be called for. At any rate, the length and sampling interval of the record should satisfy the rules of thumb governing spectral analysis (cf. Section 4.1.2.2). Ideally, in a record of discrete data, there should be no missing points. Interpolation may be used if a few data points are missing, when these are widely scattered on the record. Interpolated data should account for no more than five percent of the total data.

The following examples illustrate the use of spectral analysis in the determination of sampling frequency.

Example 1:

The wastewater influent for the city of Racine, Wisconsin, was sampled hourly in the summer of 1974 and TOC analyzed. The record is shown in Figure 4.9. The mean and variance were calculated to be 70.56 mg/L and

1262.07 mg^2/L^2 respectively. Determine the optimal sampling frequency for this plant.

The power spectrum corresponding to the record of Figure 4.9 is obtained as depicted in Figure 4.10. This power spectrum exhibits a significant peak at the 1/24 hour frequency and a less significant peak at 1/8 hour. Most of the variability on the data occurs in the frequency band from 1/48 hour to 1/16 hour. Since the last significant peak in the spectrum occurs at the 1/8 hour frequency, the sampling frequency which should be at least two times the frequency of the last significant peak, corresponding to the Nyquist frequency, should be at least 1/4 hour. In order to clearly show the 1/8 hour variability a sampling interval of 3 hours or even 2 hours is recommended in accordance with the second rule of thumb. Note that this example, the first rule of thumb stated in Section 4.1.2.2 is violated as the length of the record in Figure 4.9 (7 days) is less than 10 times the longest period of interest (one day). However, the peak at the 1/24 hour frequency is so significant that it cannot be explained by aliasing distortion alone.

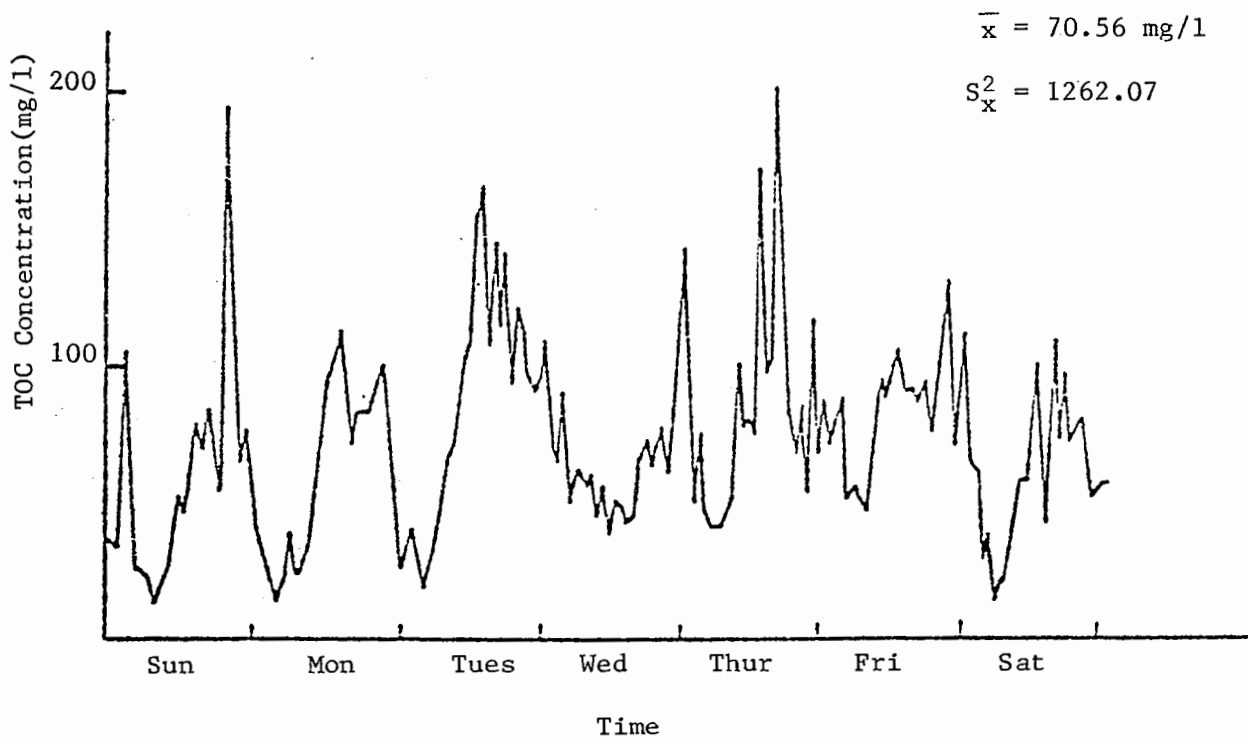


Figure 4.9 Time record of TOC of municipal wastewater at Racine, Wisconsin

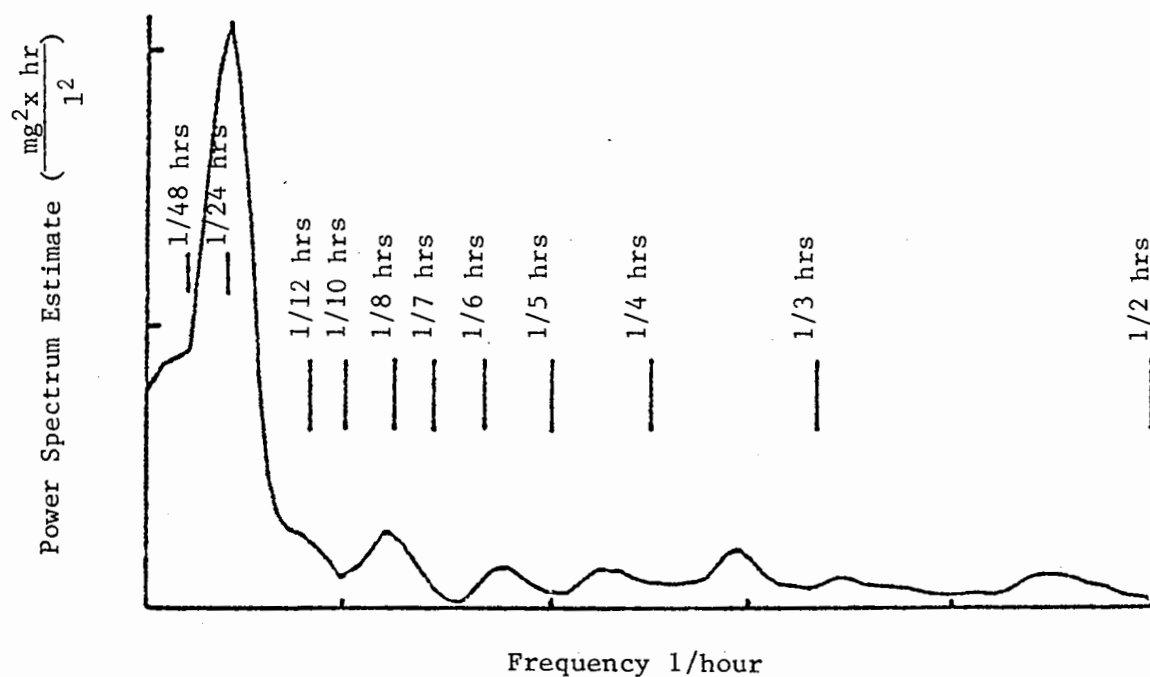


Figure 4.10 Power spectrum of TOC concentration of municipal wastewater at Racine, Wisconsin

Example 2:

The power spectra of wastewater variation corresponding to two typical types of industrial discharges are shown in Figures 4.11 and 4.12. Determine the optimal sampling frequency.

The spectrum of Figure 4.11 exhibits two strong peaks in the frequency band from 1/16 hour to 1/5 hour. This spectrum is typical for industrial plants working 24 hours a day, seven days a week, with three shifts a day. Note the absence of peaks on the low frequency region reflecting the absence of uniform, short-period cycles in the record, which would then appear to be random. Inasmuch as the last significant peak occurs between the 1/6 hour and 1/5 hour frequency, a sampling frequency of 1/2 hour is recommended (that is, 2 times 1/4 hour).

The spectrum of Figure 4.12 displays a strong peak at the 1/24 hour frequency and less significant peaks at the 1/12 hour and 1/6 hour frequencies. This spectrum is typical for industrial plants working with one daily shift. Here again, the absence of peaks in the low frequency region of the spectrum is an indication of the randomness of the record for short periods in the data. In order to clearly exhibit the 1/6 hour frequency component of the data a sampling interval of 2 hours is recommended in accordance with the second rule of thumb.

4.4 DETERMINATION OF PARAMETERS TO MONITOR

There are two statistical methods to help determine the parameters to monitor if prior regulations do not exist. The decision variable for the first method is the probability of exceeding a standard and the second is the correlation between parameters.

4.4.1 Probability of Exceeding a Standard

This method requires knowledge of:

1. The mean, μ , or sample mean, \bar{X}
2. The standard deviation, σ , or sample S.D., S_x
3. The standard, X_s , not to be exceeded for the parameter.

For normally distributed data, the probability of exceeding the standard is:

$$P(X > X_s) = P(Z > Z_\alpha) = \alpha$$

where: $Z_\alpha = \frac{X_s - \mu}{\sigma}$

After computing Z_α , the probability, α , can be found in Table 4.8. Parameters with the largest value of α have the highest sampling priority.

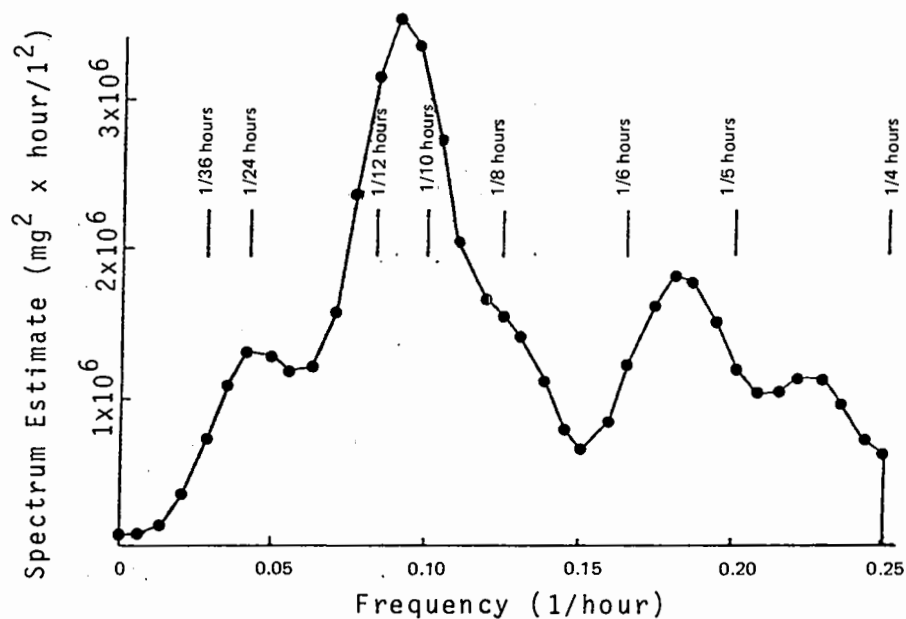


Figure 4.11 Power Spectrum of Industrial Plant Discharge, Case 1

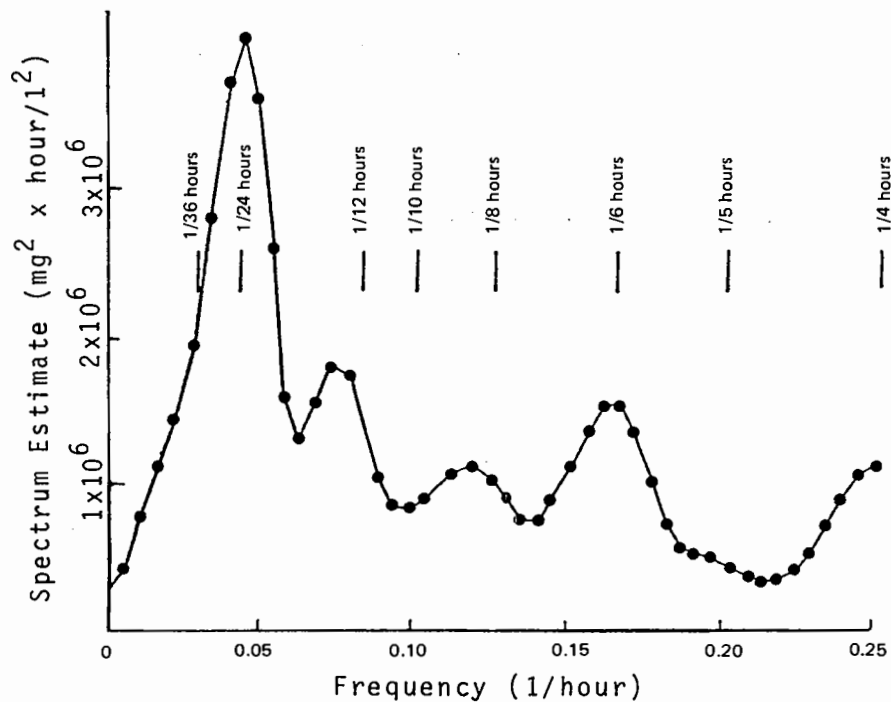


Figure 4.12 Power spectrum of industrial plant discharge, Case 2

Example 1:

The effluent standard for an industry was determined to be 100 mg/L of Cl^- . Experience has shown that the mean concentration of chlorides is 75 mg/L and standard deviation is 18 mg/L.

To determine the probability of the standard being exceeded:

1. Determine $Z_\alpha = \frac{X_s - u}{\sigma} = \frac{100 - 75}{18} = 1.39$

2. Find α from Table 4.8 such that $Z_\alpha = 1.39$. The value is 0.0823, or 8.23%.

Often effluent standards will be specified for several parameters. Then the parameters can be ranked in descending order of their probability of exceeding the standard. The priority of sampling will be in the same order. Table 4.11 is an example of how this is done.

Example 2:

The standard for another parameter is four parts per million. The average in the past was found to be 7 ppm, with a standard deviation of 2 ppm.

Here: $X_s = 4$
 $u = 7$
 $\sigma = 2$

and so: $Z_\alpha = \frac{X_s - u}{\sigma} = \frac{4 - 7}{2} = -1.5$

Because of symmetry, $P(Z < -Z_\alpha) = P(Z > Z_\alpha)$, and so, since $Z_\alpha = -1.5$ in this case, look up +1.5 in the table, finding $\alpha = 0.0668$. Since $P(Z > -Z_\alpha)$ is desired, use the fact that $P(Z > -Z_\alpha) = 1 - P(Z < -Z_\alpha) = 1 - \alpha$. So the probability of exceeding the standard is $1 - \alpha = 1 - 0.0668 = 0.9332$, or about 93.3%.

4.4.2 Correlation Between Measured Parameters (15)

Ideally, all important water quality parameters should be monitored, but since this is usually not economically feasible, a method is needed for deciding which parameters to omit. This is done by checking the closeness of correlation among parameters of interest. It is known that a correlation exists between many water quality parameters such as:

TABLE 4.11 SAMPLING PRIORITIES OF PARAMETERS FOR A TYPICAL WASTEWATER

Parameter	Water Quality Standard, X_s	Mean, \bar{X}	Standard Deviation, S	Z	$P(X > X_s)$	Sampling Priority
pH	6.5 - 8.0	7.8	0.4	0.50	0.308	5
TOC	None	31	7.9	--	0	16 - 22
COD	70	60	11	0.91	0.181	7
BOD	30	20	8	1.25	0.125	9 - 10
TKN	5	3.5	1.5	1.00	0.158	8
Phosphates	1	0.5	0.2	2.50	0.006	15
Conductivity	None	320	80	--	0	16 - 22
Total dissolved solids	500	491	125	0.072	0.472	1
Suspended Solids	30	28	5	0.40	0.34	4
Turbidity	20	19	3	0.33	0.37	3
Lead	5	3	1.0	2.0	0.0228	14
Mercury	5	2.5	1.5	1.67	0.047	13
Iron	10	7.8	1.9	1.16	0.123	11
Copper	7	0.8	0.15	1.33	0.0918	12
Alkalinity	None	--	--	--	0	16 - 22
Acidity	None	--	--	--	0	16 - 22
Calcium	None	--	--	--	0	16 - 22
Hardness	None	--	--	--	0	16 - 22
Magnesium	None	--	--	--	0	16 - 22
Total coliforms	100	81	65	0.29	0.386	2
Fecal coliforms	10	5	64	1.25	0.125	9 - 10
Chlorides	200	156	59	0.90	0.134	6

BOD₅ and TOC
 COD and TOC
 Chlorides and Conductivity
 Total Dissolved Solids and Conductivity
 Suspended Solids and Turbidity
 Acidity, Alkalinity and pH
 Hardness, Calcium and Magnesium
 Hardness and Alkalinity

If a strong correlation exists between two or more parameters, the monitoring of one parameter may be discontinued or monitored at a reduced frequency. In order to apply the technique, the following must be available:

1. A data record for all parameters of interest
2. A computer program for calculating correlation coefficients.

The relationship between two variables X and Y can be linear or non-linear (such as exponential, logarithmic or random). If a non-linear relationship exists, attempt to linearize the relationship, by using logarithms of the values of X and Y, or some other functional approximation. Then linear regression analysis provides a linear approximation of the form $\hat{Y} = a + b\hat{X}$. The coefficient of correlation, R_{XY} , will then be a measure of the closeness of fit. The coefficient of correlation is determined from the equation:

$$R_{XY} = \frac{\sum_{i=1}^N (X_i - \bar{X})(Y_i - \bar{Y})}{\left[\sum_{i=1}^N (X_i - \bar{X})^2 \sum_{i=1}^N (Y_i - \bar{Y})^2 \right]^{1/2}}$$

Numerous computer package subroutines are available for the above analysis.

The hypothesis that a relationship exists between X and Y can be tested at a given level of significance α (where $1 - \alpha$ is the confidence that the hypothesis is true). If the obtained coefficient of correlation is such that $|R_{XY}| > R_c$, where R_c is the minimal correlation coefficient, which can be found in Table 4.12, the null hypothesis (that the correlation is zero) is rejected.

If a pair of parameters has a correlation coefficient significantly greater than the value from the table, one parameter in the pair is eligible for elimination from or reduction of monitoring. The decision on which a parameter should be eliminated will be based on the cost of data acquisition and the priority of the parameter.

Example:

A wastewater system was surveyed for an extended period of time. As a

TABLE 4.12 VALUES OF CORRELATION COEFFICIENT, r , FOR
TWO LEVELS OF SIGNIFICANCE (16)

Degrees of Freedom $n = N - 1$	Percent Level of Significance, α	
	Five	One
1	0.997	1.000
2	0.950	0.990
3	0.878	0.959
4	0.811	0.917
5	0.754	0.874
6	0.707	0.834
7	0.666	0.798
8	0.632	0.765
9	0.602	0.735
10	0.576	0.708
11	0.553	0.684
12	0.532	0.661
13	0.514	0.641
14	0.497	0.623
15	0.482	0.606
16	0.468	0.590
17	0.456	0.575
18	0.444	0.561
19	0.433	0.549
20	0.423	0.537
21	0.413	0.526
22	0.404	0.515
23	0.396	0.505
24	0.388	0.496
25	0.381	0.487
30	0.349	0.449
35	0.325	0.418
40	0.304	0.393
45	0.288	0.372
50	0.273	0.354
60	0.250	0.325
70	0.232	0.302
80	0.217	0.283
90	0.205	0.267
100	0.195	0.254
125	0.174	0.228
150	0.159	0.208
200	0.138	0.181
300	0.113	0.148
400	0.098	0.128
500	0.088	0.115

result of the survey, 25 sets of wastewater quality data were gathered. Each set contained data on pH, TOC, COD, BOD, TKN, phosphorus, conductivity, total dissolved solids, suspended solids, turbidity, lead, mercury, iron, copper, alkalinity, acidity, hardness, calcium, magnesium, coliform bacteria, fecal coliform and chlorides.

1. Determine the sampling priority of each parameter.
2. Determine which parameter measurements can be eliminated or reduced.

First, the probability exists that a parameter will exceed its standard. This will determine the sampling priority of the standard.

The correlation analysis of the 22 parameters in Table 4.11 was performed by a computer, using the formula given previously. From Table 4.12, it was determined that:

$$R_c = \begin{cases} 0.388 & \text{for } \alpha = .05 \\ 0.496 & \text{for } \alpha = .01 \end{cases}$$

Table 4.13 shows the results of the analysis.

Sampling for total dissolved solids (TDS) has the highest priority, but, because of the high correlation between TDS and conductivity, analyses for conductivity need not be considered. Total coliforms have the second highest priority, but since the correlation between total and fecal coliforms is high, analyzing for fecal coliforms is not necessary. The high correlation among BOD, COD and TOC makes it possible to eliminate or reduce one or two of them. Testing for turbidity could also replace that for suspended solids. It is also possible to eliminate at least one analysis from the group hardness, coliform and alkalinity. Metals have relatively low priority and so at least one of them can be reduced. Thus, the following streamlined program is feasible:

<u>Parameter</u>	<u>Priority of Sampling</u>
pH	high
TOC or COD	high
BOD	reduced
TKN	high
Phosphates	reduced
Total Dissolved Solids	high
Suspended Solids or Turbidity	high
Lead	reduced or not necessary
Mercury	reduced or not necessary
Iron	reduced
Copper	reduced or not necessary
Alkalinity	reduced
Hardness	reduced
Total Coliforms	high
Fecal Coliforms	reduced or not necessary

TABLE 4.13 MATRIX OF CORRELATION COEFFICIENTS

Parameter	pH	TOC	COD	BOD ₅	TKN	P	Cond	TDS	SS	T	Pb	Hg	Fe	Cu	Alk	Ac	Ca	Hard	Mg	Tc	FC	Cl
pH	--																					
TOC	0	--																				
COD	0	0.8	--																			
BOD ₅	0	0.68	0.63	--																		
TKN	0	0	0.15	0.18	--																	
Phosp	0	0	0.18	0.21	0.69	--																
Conduct	0	0.30	0.41	0.35	0.33	0.17	--															
TDS	0	0.25	0.35	0.48	0.41	0.20	0.91	--														
SS	0	0.25	0.40	0.38	0.25	0.75	0.10	0.18	--													
Turb	0	0.4	0.51	0.33	0.18	0.68	0.18	0.59	0.89	--												
Pb	0.18	0	0	0	0	0	0.28	0.31	0.18	0.15	--											
Hg	0	0	0	0	0	0	0.30	0.23	0.25	0.31	0.70	--										
Fe	0.1	0	0	0	0	0	0.41	0.39	0.58	0.61	0.18	0.23	--									
Cu	0	0	0	0	0	0	0.30	0.25	0.31	0.25	0.69	0.59	0.41	--								
Alk	0.6	0	0	0	0	0	0.38	0.41	0	0	0	0	0	0	--							
Acid	0.6	0	0	0	0	0	0.20	0.15	0	0	0	0	0	0	0.49	--						
Ca	0	0	0	0	0	0	0.31	0.35	0	0	0	0	0	0	0.65	0	--					
Hard	0.1	0	0	0	0	0	0.61	0.68	0	0	0	0	0	0	0.61	0.18	0.88	--				
Mg	0	0	0	0	0	0	0.40	0.31	0	0	0	0	0	0	0.18	0	0.35	0.18	--			
T. Coll	0	0.31	0.35	0.38	0	0	0	0	0.12	0.11	0	0	0	0	0	0	0	0	0	--		
F. Coll	0	0.10	0.18	0.21	0	0	0	0	0.11	0.08	0	0	0	0	0	0	0	0	0	0.79	--	
Chlor	0	0	0	0	0	0	0.58	0.88	0	0	0	0	0	0	0	0	0	0	0	0	0	--

0 = no engineering relevance; assumed no relation.

4.5 IN-PLANT SAMPLING AND NETWORK MONITORING

If the sampling locations have not been predetermined, there are systematic methods of determining the location of sampling points. However, these methods are only tools to aid sampling personnel and do not replace professional judgment and experience.

4.5.1 Segmentation - Priority Technique

This technique can be applied to any large flowing network including an industrial plant collection system, a municipal sewerage system, or even a watershed network. To apply this technique the following information must be known at a node j between segment points A and B:

1. The mass flow rate of the parameter of interest ($Q_j C_j$), where Q = volumetric flow rate, C = concentration
2. The range of variation of the parameter input $p_j = (Q_j C_j)_{\max} - (Q_j C_j)_{\min}$.
3. The approximate frequency of the fluctuations, P_j .
4. Values for the coefficient of transformation through each segment β_{AB} .
5. Values for the reduction in variation through each segment, α_{AB} .

Segmentation of the system is done by first isolating the locations which modify the waste stream condition, such as junctions of wastewater treatment units, overflows, stormwater inflow, sidestreams, or lateral sewers. An example of a municipal wastewater system segmentation is shown in Figure 4.13. The system has 16 segments, 12 inside the waste system and four on the receiving water body. In an ideal situation, sampling stations can be located in all segments of the system. With a limited budget, however, the number of sampling points will be limited. Therefore, there is a necessity for a measure to establish priorities of sampling for each segment. The measure can be the correlation coefficient between the segments. If a high correlation exists for the measured parameter between two segments, one can rely on measurement of the parameter in only one segment and sampling of the other segment is not necessary. Unlike the large river monitoring systems, wastewater systems have at least one fixed location of a monitoring point, such as the influent and/or effluent of a treatment plant. Using the correlation analysis between the monitored segment and other upstream and downstream segments, it is possible to identify segments with low correlation to the monitored segment. A second consideration should be the worth of the data measured at the segment. For example, if the magnitude of a measured parameter and its variability are insignificant when related to other segments, the segment will have a low priority for monitoring.

4.5.1.1 First Priority Sampling Points

The location of at least one sampling point is strictly determined by the basic objectives of a monitoring program, i.e. protection of the

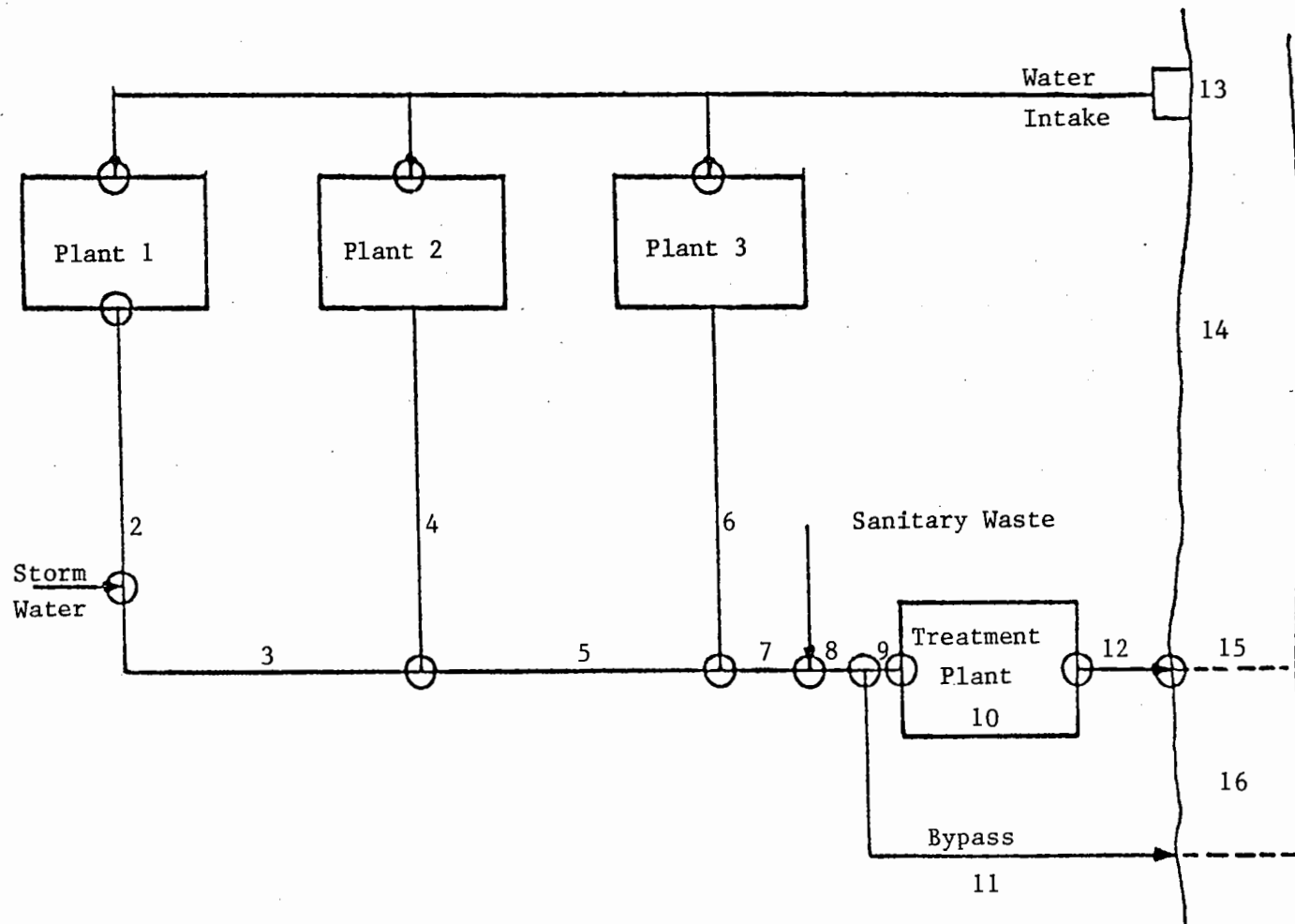


Figure 4.13 Segmentation of a wastewater system

environment. This objective requires that a sampling point be located just before a wastewater discharge to a receiving water body. If the industry has several wastewater outfalls, a sampling point should be located downstream from the last outfall. In the case that the monitoring point is located in the receiving water body, an upstream station to monitor the upstream water quality and quantity is necessary. This will allow the effect of the wastewater discharge on the receiving water body to be clearly identified. If the water intake for the industry is situated on the same water body, the upstream sampling point can be conveniently located at the water intake.

4.5.1.2 Second Priority Sampling Points

Other important objectives of a sampling program can be to monitor the quality of raw wastewater and to evaluate the efficiency of a treatment process. Thus, a location for a second priority sampling point would normally be at the influent to a treatment plant.

For small and medium sized wastewater systems, sampling at the first and second priority sampling points should be sufficient to meet most of the objectives and requirements established by regulatory agencies.

4.5.1.3 Third Priority Sampling Points

The location of additional sampling points may be necessary for large wastewater systems with many inputs. Their purpose is to provide additional information or warning. In this case, the method of segmenting the wastewater system and determining sampling priorities for each segment can be of use in establishing additional sampling points. Segmentation of a wastewater system is accomplished by isolating the locations which substantially modify the waste stream conditions. These locations include junctions of wastewater streams, treatment units, wastewater overflow, flow dividers, storm and cooling water inflows, and storage reservoirs. The following outlines a method of segmentation.

1. It is best to represent the wastewater system by a linear graph technique. Such a graph consists of nodes or junctions and branches or lines. All wastewater inputs will enter the system through the nodes, and the nodes also separate branches with different characteristics. A branch is considered as a segment with uniform geometric, hydraulic, and transform characteristics. The following depicts the classification of some typical elements of a wastewater system.

Nodes - manholes, changes of slope, changes in conduit diameter, flow dividers, junctions of sewers and channels, outfalls, influents and effluents to treatment steps, etc.

Branches - conduits, channels, treatment steps, bypasses, adjacent receiving water bodies, storage reservoirs, holding ponds, and so on.

For the industrial water/wastewater system of Figure 4.14, a linear

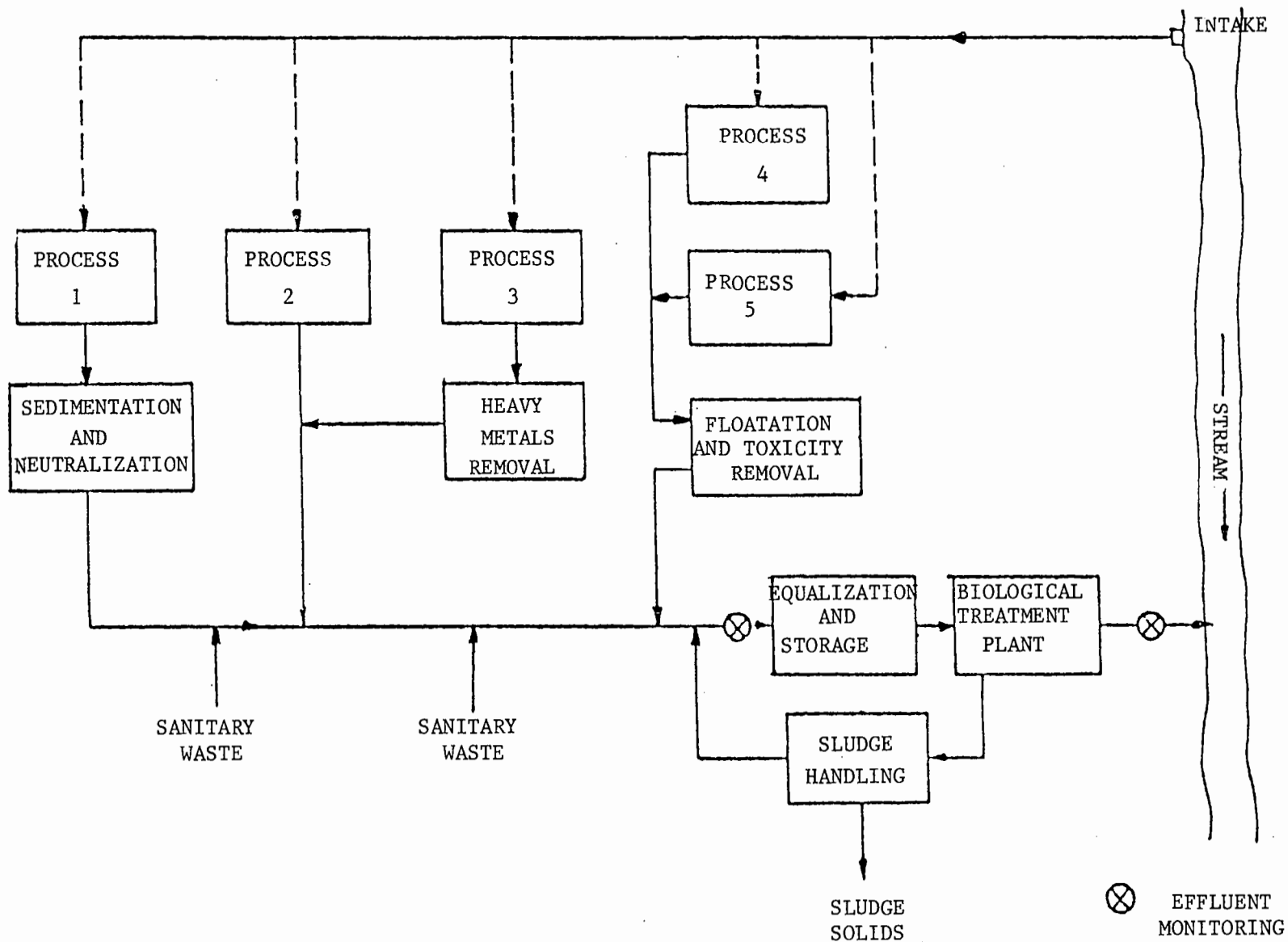


Figure 4.14 An industrial water/wastewater system

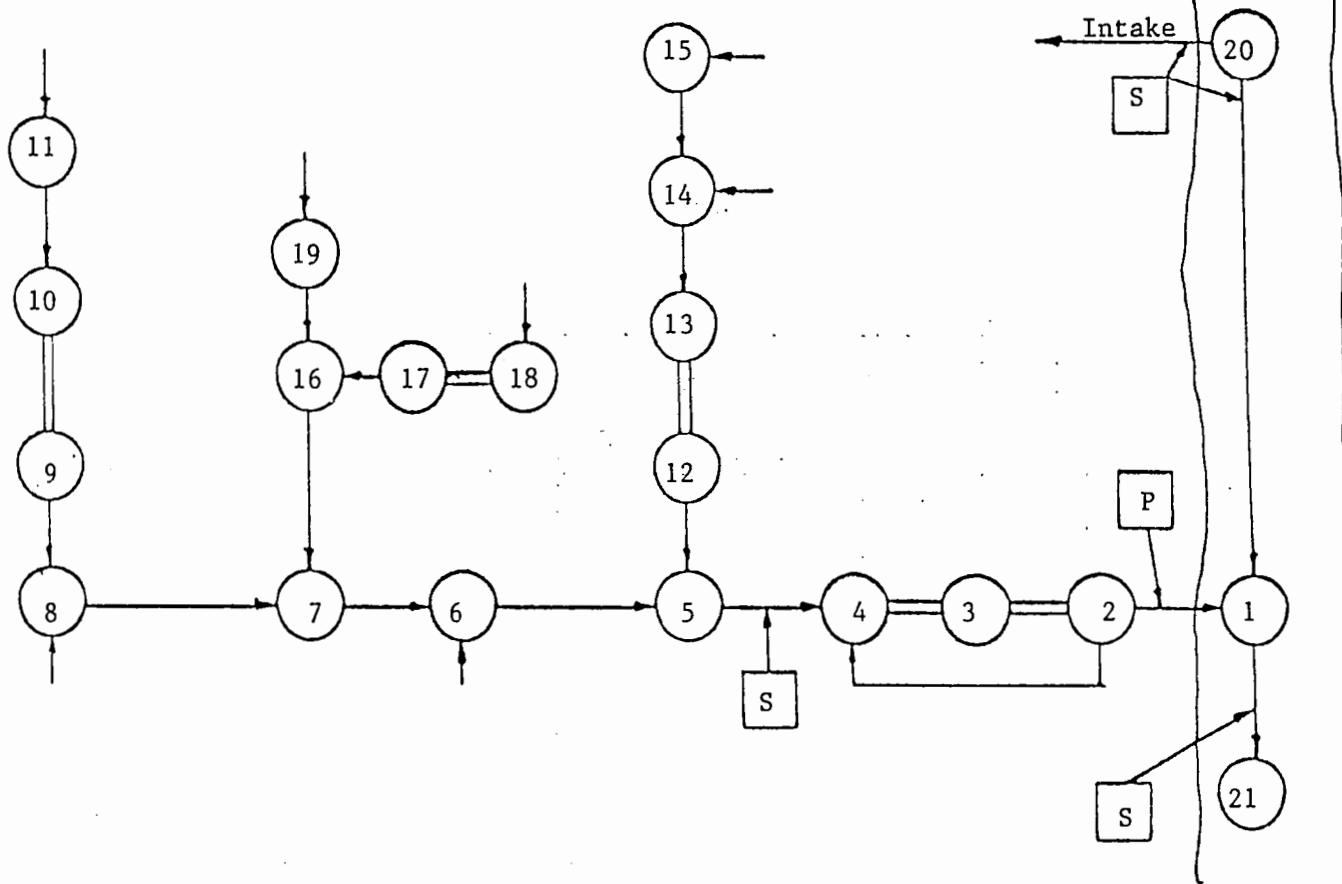
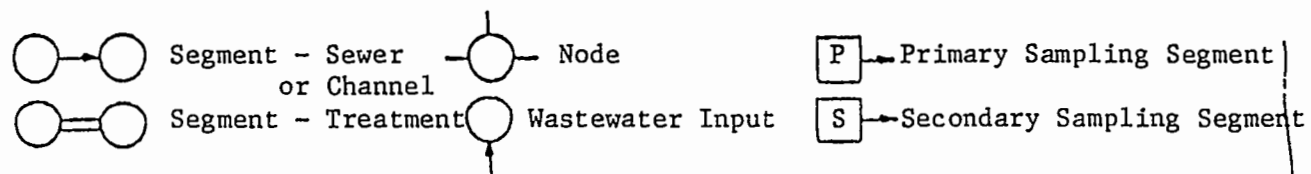


Figure 4.15 Linear graph representation of the system

graph representation is shown in Figure 4.15.

2. In segmenting the system, each node should be uniquely numbered. Wastewater input to each node should be characterized by the range of variation:

$$P_j = (Q_j C_j)_{\max} - (Q_j C_j)_{\min},$$

which is, basically, the range of waste loads to the node j .

The units of P_j will be g/sec if the flow Q is expressed in m^3/sec and concentration C in mg/L. It might be convenient also to know the approximate frequency of fluctuations of the input P_j .

A node table should be prepared such as is shown in the following example (Table 4.14).

3. Each branch is identified by a double subscript AB , where A is the number of the upstream node and B is the number of the downstream node.

Coefficients of transformation β_{AB} and α_{AB} should be assigned for each branch. The coefficient of transformation β_{AB} describes roughly how the variability of the wastewater is reduced in this segment. In most cases β_{AB} can be determined approximately from the geometry of the segment and treatment parameters. The coefficient α_{AB} describes how the correlation is reduced in the segment. The following values of the coefficients are recommended:

	<u>Let $\beta_{AB} =$</u>	<u>Let $\alpha_{AB} =$</u>
• Short sewers and channels	1.0	1.0
• Plug flow treatment steps, long sewers and channels with decay	$\exp(-KT)$	0.9 to 1.0
• Completely mixed treatment steps with short detention time ($t \ll 1/f$)	$1 - E_{tr}/100$	0.85 to 0.95
• Completely mixed treatment steps with long detention time ($t \gg 1/f$)	$\left[2(1+Kt)tf\right]^{-\frac{1}{2}}$	$(2tf)^{-\frac{1}{2}}$
• Storage and equalization reservoirs and holding ponds with no decay	$(2tf)^{-\frac{1}{2}}$	$(2tf)^{-\frac{1}{2}}$

where:

K = decay coefficients in the segment (in units of day⁻¹)
t = detention time in the segment (in days)
f = frequency of fluctuations of waste inputs
E_{tr} = treatment efficiency (in percent)

4. Determine and approximate ranges of wastewater quality variations for each segment. This can be done by starting at the most upstream nodes containing wastewater inputs and moving downstream, by the buffering capacity of segments and by new wastewater inputs (such as process discharges) in downstream nodes.

Figure 4.16 illustrates how this procedure is accomplished. JK is the most upstream node containing a wastewater input and would therefore be the starting point. The range of wastewater variability will be

$$r_{JK}^J = P_j \quad \text{where } r_{JK}^J \text{ is the wastewater quality}$$

variation range in segment JK downstream from J. Above, the downstream node K the variation range is determined by

$$r_{JK}^K = r_{JK}^J \times \beta_{JK}$$

At a node the variability range can be changed by wastewater inputs to the node and by other upstream branches entering the node. For a case where more than one input enters a node, the following relationship (propagation of errors) can be used to compute the variability range:

$$r_{AB}^A = \left[\sum_i \left(r_{iA}^A \right)^2 + \sum_j \left(P_{jA} \right)^2 \right]^{\frac{1}{2}}$$

where A denotes the node under consideration, B denotes the node immediately downstream from A, iA represents the ith upstream branch entering node A, and jA represents the jth wastewater input entering node A. In Figure 4.16, the above formula is used for node L.

The variability ranges for all segments in a network can be computed using the relationship described above and shown in Figure 4.16. It is recommended that the variability range be checked by known data from a survey or monitoring. The above procedure should give adequate results assuming that all inputs to the system are random and uncorrelated to each other.

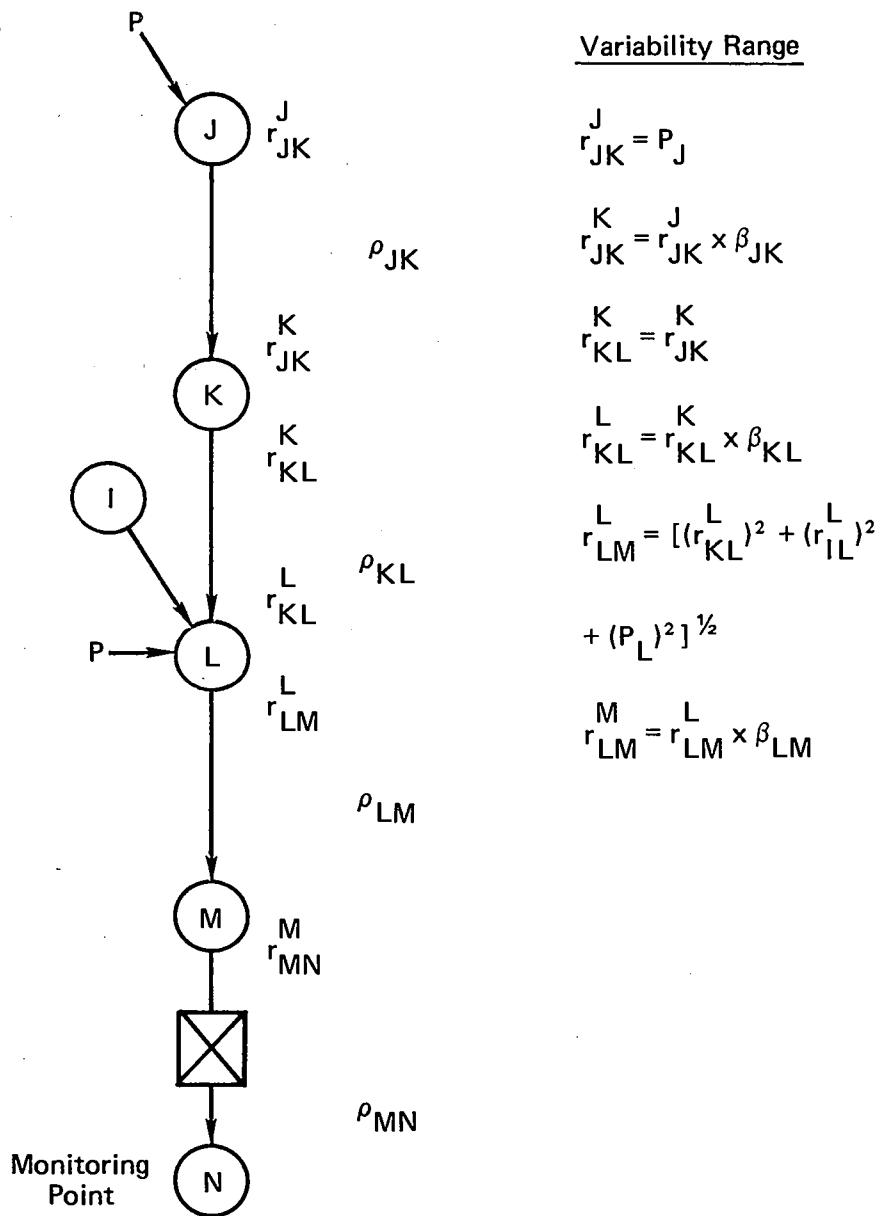


Figure 4.16 Estimation of variability and correlation in segments

5. Determine the approximate correlation coefficient between each segment's water quality variations and variations in the monitored segment. The correlation coefficient, r_{MN} , for the monitored segment itself equals 1.0. Moving further downstream or upstream causes the correlation coefficient to decrease as the relation between the wastewater fluctuations in the monitored segment and the segment downstream or upstream diminishes. The change in the correlation coefficient can be roughly estimated as follows:

In a Branch - multiply ρ by the coefficient

In a Node - multiply ρ by the ratio r_{AB}^B / r_{BC}^B

where B is the node under consideration, AB is the branch located farther away from the monitored segment, and BC is the branch located closer to the monitored segment.

6. Additional sampling points should be located at the segment where, theoretically, the correlation with the monitored point ends. Since the correlation influence of both points extends both downstream and upstream, there will be an overlap such that each sampling point will have an influence of $r = \sqrt{R_c}$, where R_c is the critical point found in Table 4.12. If the number of samples is now known, a value of R_c between 0.25 and 0.30 will give a good estimate.
7. If there are several segments to be monitored, that is, one or more segments have a correlation level less than R_c , the priority can be determined according to the magnitude of the variability range r_{ij} for the segment ij . The segment with the highest r_{ij} will have the highest priority.
8. Once a new sample location is established, the procedure is repeated to find the next sampling location.
9. The entire procedure should be repeated for each important parameter.

Example:

Determine the locations of sampling points for the wastewater system given in Figure 4.14. The analysis will be based on the COD information representing the organic load to the system.

Step 1 - Divide the system into segments using the linear graph representation, as in Figure 4.15.

TABLE 4.14 WASTEWATER LOADS TO NODES
CONSTITUENT: COD

Node	Maximal Loading g/sec	Minimal Loading g/sec	Pj
1	0	0	0
2	0	0	0
3	0	0	0
4			
5	0	0	0
6	10	1.2	8.8
7	0	0	0
8	30.0	6.0	24.0
9	0	0	0
10	0	0	0
11	175.0	100.0	75.0
12	0	0	0
13	0	0	0
14	66.0	17.0	49.0
15	109.0	21.0	88.0
16	0	0	0
17	0	0	0
18	42.0	23.0	19.0
19	121.50	93.0	28.5

Fluctuations of maximum and minimum at most nodes - $1/8 \text{ hours}^{-1}$

TABLE 4.15 COEFFICIENTS OF VARIATION IN BRANCHES

Branch	Description	β	α
1-2	Effluent Channel	1.0	1.0
2-3	Activated Sludge Plant	0.1	0.4
3-4	Equalization Basin	0.2	0.2
4-5	Sewer	1.0	1.0
5-6	Sewer	1.0	1.0
6-7	Sewer	1.0	1.0
7-8	Sewer	1.0	1.0
8-9	Sewer	1.0	1.0
9-10	Neutralization Plant	0.9	0.9
10-11	Sewer	1.0	1.0
5-12	Sewer	1.0	1.0
12-13	Floatation Unit	0.5	0.5
13-14	Sewer	1.0	1.0
14-15	Sewer	1.0	1.0
7-16	Sewer	1.0	1.0
16-17	Sewer	1.0	1.0
17-18	Chemical Coagulation	0.7	0.7
16-19	Sewer	1.0	1.0

- Step 2 - Locate a first priority sampling point (P) at the effluent channel (segment 1-2). Locate second priority sampling points (S) at the influent to the treatment plant (segment 4-5) and in the receiving water body, upstream and downstream from the waste discharge.
- Step 3 - Estimate the variability range of the inputs to the system (Table 4.14).
- Step 4 - Estimate β and α for each segment (Table 4.15).
- Step 5 - Estimate the variation range in each segment. Proceed upstream from the most downstream segment (Table 4.16).
- Step 6 - Estimate the coefficient of correlation between wastewater variations in each segment and the nearest monitored segment to segment 4-5. Proceed from the monitored segment (where $R = 1.0$) and work upstream (Table 4.16 right portion). Each segment is correlated to the segment immediately downstream toward the monitored point. Developing a correlograph (Figure 4.17) at this stage will aid in the decision process in Step 7.
- Step 7 - Once the correlation coefficients are estimated, find those where $R_c < R_c$, with R_c estimated to be 0.30. Based on this criterion, the priority for monitoring the upstream segments will usually have a high correlation and, therefore, only one segment needs to be monitored. The second criterion is the magnitude of the variability, r_{ij} , for the segments with low correlation levels. Both the values of R and of r_{ij} should be examined for these segments, the requirements and objectives of the program should be considered, and then professional judgment must be exercised.
- In this example, segments 17-18, 16-17 and 16-19 are neighboring segments with low correlation levels. Looking at the variability values, it is obvious that segment 16-19 has the highest value, indicating the great fluctuations in wastewater quality. Therefore, of these three, segment 16-19 might have the highest priority. Segments 14-15, 13-14 and 12-13 are also neighboring segments with low correlation levels. Segment 13-14 has the greatest variability and would therefore be chosen. Since its variability is much higher than that of segment 16-19, it would have the highest overall priority. At this stage, correlation and variability values can be recalculated to see if monitoring at these points would satisfy the program requirements. If not, the procedure should be repeated.

4.5.2 Probability of Exceeding a Standard (17)

In locating sampling points in a receiving water body, the probability of exceeding a receiving water standard should be considered. For all conservative substances and all nonconservative substances except oxygen and possibly temperature and nitrates, the critical section would be located immediately downstream from the outfall. The section with the highest probability of violating the dissolved oxygen standard will be further downstream near the "sag point". The location of the critical point can be

TABLE 4.16 DETERMINATION OF THE SAMPLING PRIORITIES OF SEGMENTS

Segment	Upstream variation range $r_u = (\sum r^2 + \sum p^2)^{0.5}$	Downstream variation range $r_d = r_u * \beta$	Correlation coefficient in the branch		Priority for tertiary monitoring
			at the downstream node $P_u = P_d \frac{r_u}{r_d}$	at the upstream node $p = p \alpha$	
16-19	28.5	28.5	$0.33 * 28.51/31.45 = 0.30$	0.30	T2
17-18	19.0	$19 * 0.7 = 13.3$	0.14	0.14 0.7 = 0.10	T3
16-17	13.3	13.3	$0.33 * 13.3/31.45 = 0.14$	0.14	
7-16	$(28.5^2 + 13.3^2)^{0.5} = 31.45$	31.45	$0.81 * 31.45/78.24 = 0.33$	0.33	
10-11	75	75	0.63	0.63	
9-10	75	$75 * 0.9 = 67.5$	0.70	$0.7 * 0.9 = 0.63$	
8-9	67.5	67.5	$0.75 * 67.5/71.64 = 0.70$	0.70	
7-8	$(67.5^2 + 24^2)^{0.5} = 71.64$	71.64	$0.81 * 71.64/78.24 = 0.75$	0.75	
6-7	$(71.64^2 + 31.45^2)^{0.5} = 78.24$	78.24	$0.82 * 78.24/78.73 = 0.81$	0.81	
5-6	$(78.24^2 + 8.8^2)^{0.5} = 78.73$	78.73	$1.0 * 78.73/96.12 = 0.82$	0.82	
14-15	88.0	88.0	$0.26 * 88/100.72 = 0.23$	0.23	
13-14	$(88^2 + 49^2)^{0.5} = 100.72$	100.72	0.26	0.26	T1
12-13	100.72	$100.72 * 0.5 = 50.36$	0.52	$0.52 * 0.5 = 0.26$	
5-12	50.36	50.36	$1.0 * 50.36/46.12 = 0.52$	0.52	
4-5	$(78.73^2 + 50.36^2)^{0.5} = 96.12$	96.12	1.0	1.0	Initial segment monitoring

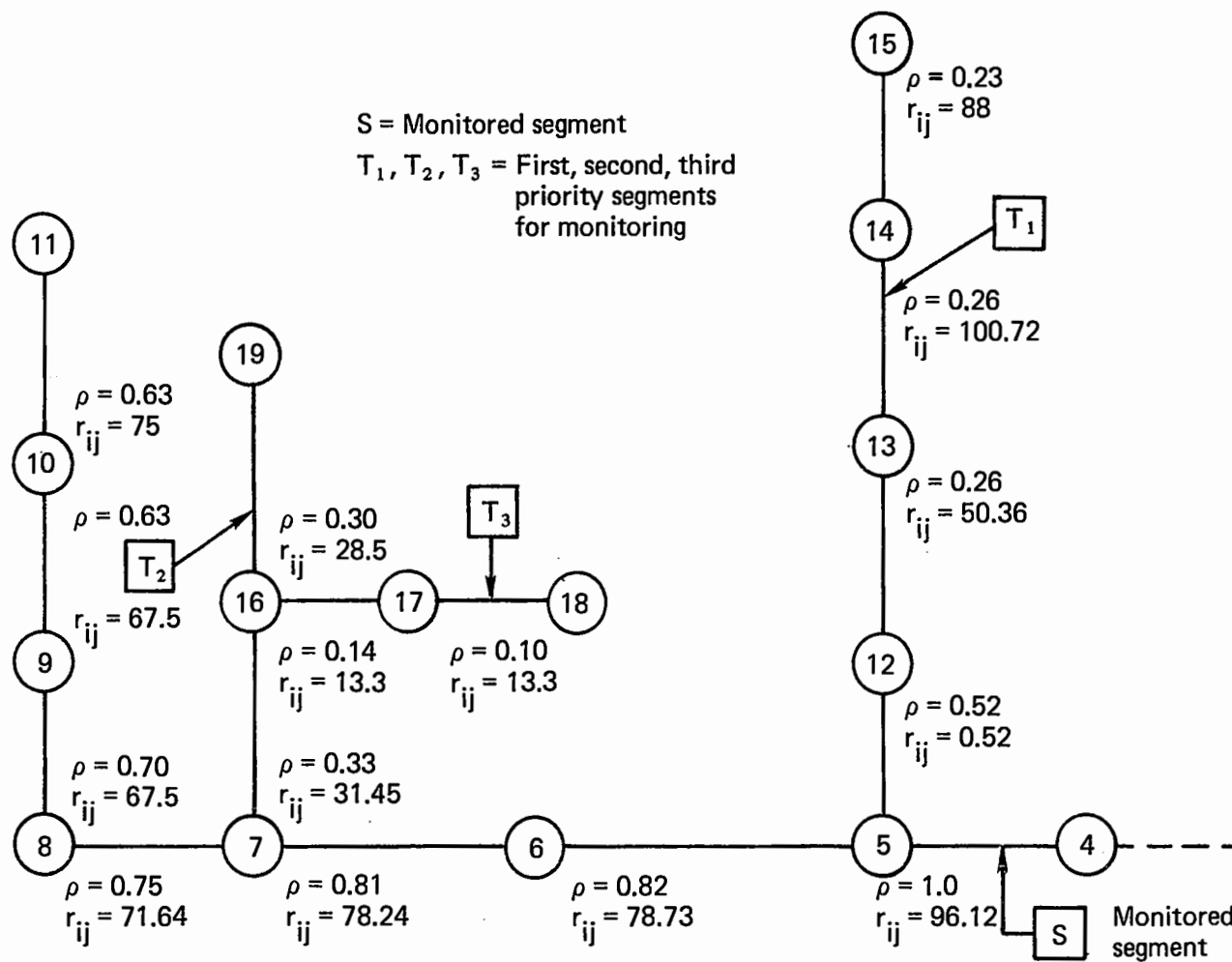


Figure 4.17 Correlograph for segments

approximately evaluated as follows:

The probability that the dissolved oxygen standard will be exceeded is:

$$P(C < C_s) = P(D > D_s) = P > Z \left(Z_s = \frac{D_s - \overline{D(x)}}{S(x)} \right)$$

which can be found in Table 4.9, where:

C is the dissolved oxygen concentration

C_s is the dissolved oxygen standard

D is the oxygen deficit

D_s is the maximum allowable oxygen deficit

$$D(x) = \left(\frac{K_1 L_0}{K_2 - K_1} \right) \exp \left[\left(\frac{-K_1 x}{u} \right) - \exp \left(\frac{-K_2 x}{u} \right) \right] + D_0 \exp \left(\frac{-K_2 x}{u} \right)$$

which is the average oxygen deficit at distance x from the outfall $S(x) = A_1 \times S_{L_0} \times u$ is the standard deviation at distance x. (15 to 17)

$\overline{L_0}$ is the average BOD discharge

S_{L_0} is the S.D. of the BOD discharge

K_1 is the coefficient of deoxygenation

K_2 is the coefficient of re-aeration

D_0 is the initial oxygen deficit

u is the stream velocity

$$A_1 = \frac{K_1}{K_2 - K_1} \left[\exp \left(\frac{-K_1 x}{u} \right) - \exp \left(\frac{-K_2 x}{u} \right) \right]$$

To find a maximal $P(C < C_s)$, it is sufficient to find a location x such that $Z_s = (D_s - \overline{D(x)})/S(x)$ is a minimum. This can be accomplished by finding the location x at which $\overline{D(x)}/S(x)$ is a maximum (and so $P(D(x) > D_s)$ is a maximum. The distance x can be found by plotting $\overline{D(x)}/S(x)$ against x for given K_1 , K_2 , D_0 , L_0 and u, and then finding the x value corresponding to the highest value of $\overline{D(x)}/S(x)$.

4.6 REFERENCES

1. Haber, Audrey and Richard P Runyon. "General Statistics". Reading, Massachusettes Addison-Wesley, 1969.
2. Bendat, J. S. and A.G. Peirsol. "Random Data: Analysis & Measurement Procedures". New York, Wiley-Interscience, 1971.
3. Dixon, W.J. "BMD Biomedical Computer Programs. University of California Press. Berkley, California 1973.
4. Barr, A.J., J.H. Goodnight, J.P. Sall, and J. T. Helwig. "Spectra Procedure, in a User's Guide to SAS 76". SAS Institute, Inc. Raleigh, North Carolina., 1976.
5. Hogg, Robert V. and Allen T. Craig. "Introduction to Mathematical Statistics, 3rd Edition". London, The Macmillan Company, 1970
6. Foster, H.A. "Theoretical Frequency Curves and Their Application to Engineering Problems". Trans. ASCE Paper, 1523, p. 142-173, 1924.
7. Associated Water & Air Resources Engineers, Inc. "Handbook for Industrial Wastewater Monitoring". U.S. EPA Technology Transfer, 8-8 to 8-12, August 1973.
8. Sparr, T.M. and R.W. Hamm Jr. "Variations of the Municipal Waste Effluent Quality and the Implications for Monitoring". Proc. of the International Seminar and Exposition on Water Resources Instrumentation, Chicago, June 4-6, 1974 Water Resources Instrumentation, Volume 1: Measuring and Sensing Methods". Ann Arbor Science Publishers, Inc. Ann Arbor, Michigan, 1974.
9. Owen, Donald, B. "Handbook of Statistical Tables". Addison-Wesley Company, Reading, Massachusetts. 1962.
10. Montgomery, H.A.C. and I.C. Hart. "The Design of Sampling Programs for Rivers and Effluents". Water pollution Control (London, England), 73: 77-98, 1974.
11. Drobny, N.L. "Monitoring for Effective Environmental Management". Proc. ASCE National Water Resources Engineering Meeting. Atlanta, Georgia, January 24-28, 1972.
12. Gunnerson, C.G. "Optimizing Sampling Intervals". Proc. IBM Scientific Computing Symposium, Water and Air Resources Management. White Plains, New York, 1968.

13. Sparr, T.M. and P.J. Schaezler. "Spectral Analysis Techniques for Evaluating Historical Water Quality Records". Proc. of the International Seminar and Exposition on Water Resources Instrumentation, Chicago, June 4-6, 1974. Volume 2: Data Acquisition and Analysis. Ann Arbor Science Publishers, Inc. Ann Arbor Michigan, 1974.
14. Wastler, T.A. "Application of Spectral Analysis to Stream and Estuary Field Studies". U.S. Department of HEW, Cincinnati, Ohio, p 27, November, 1963.
15. Kaester, R.L., J.J. Cairns, and J.S. Crossman. "Redundancy in Data from Stream Surveys". Water Research. 8: 637-642, August 1974.
16. Fisher, R.A. and F. Yates. "Statistical Tables for Biological, Agricultural and Medical Research". London, Oliver and Boyd, 1949.
17. Chamberlain, S.G., C.V. Beckers, G.P. Grimsrad, and R.D. Shull. "Quantitative Methods for Preliminary Design of Water Quality Surveillance Systems". Water Resources Bulletin, 10: 199-219, April, 1974.

CHAPTER 5

SAMPLING MUNICIPAL WASTEWATERS

5.1 BACKGROUND

Municipal wastewaters are collected and treated by chemical, physical, and/or biological means prior to discharge to surface waters. Up to three stages, primary, secondary and tertiary, are commonly used at municipal treatment plants.(1) The wastewater characteristics vary with the size and habits of the community, the type of collection system (combined or separate), the amount of infiltration and the volume and type of industrial discharges entering the system.

5.2 OBJECTIVES OF SAMPLING PROGRAMS

5.2.1 Regulatory

Sampling of municipal wastewaters is required by regulatory agencies for the NPDES permit program. The location of sampling points, frequency, sample type, and the like are specified in the NPDES permit.

5.2.2 Process Control

In addition, sampling is performed at municipal treatment plants for process control. This monitoring provides a check on the efficiency of the process allowing the operator to make adjustments to optimize the process efficiency.

5.2.3 Research and Development

The special needs of research projects dictate the sampling program. Each project must be considered individually and no general guidelines can be given.

5.3 FREQUENCY OF SAMPLING

5.3.1 Established by Regulation

Follow the frequency requirements in the permit issued by the regulatory agencies.

5.3.2 Use of Statistics

Apply spectral analysis techniques (Section 4.3.1) to establish the optimum frequency. If the data required for this technique are not available:

1. Conduct a week-long survey collecting hourly samples. For combined municipal and industrial wastewaters choose a week of high industrial production.
2. Determine if any unusual industrial or community discharge occurred during the sampling period, for example, an extensive spill or extremely heavy rainstorm, which may invalidate the data and necessitate a repeat of the survey.

After data collection, the analysis of data should be performed as outlined in Section 4.3.1.

5.3.3 Compliance Purposes

The NPDES Compliance Sampling Manual (2) indicates that sampling programs must include a minimum of a 24 hour of operating day composite supplemented by two or more grab samples. With highly variable wastewater characteristics or flow rate changes, additional sampling is required. A composite sample is defined as a minimum of eight discrete samples taken, proportional to flow rate, over the compositing period.

5.3.4 Other Considerations

Follow interim sampling frequencies prior to the generation of data for statistical analysis. Frequencies appear in Tables 5.1 (3) and 5.2.(4)

5.4 LOCATION OF SAMPLING POINTS

Collect the sample at the location(s) specified in the permit. At these locations collect the sample in the center of the channel at 0.4 to 0.6 depth where the flow is turbulent, well mixed, and the settling of solids is minimal. Sampling at 0.4 to 0.6 depth will avoid skimming of the water surface or dragging the channel bottom.

For BOD analyses, collect the samples prior to disinfection.(5) For BOD and suspended solids, samples of plant influent and effluent must be collected in order to calculate the removal of these constituents. The sampling of wastewater for immiscible liquids, such as oil and grease, requires special attention and no specific rule can be given for selection of the most representative site because of wide range of conditions encountered in the field. In such cases, experience of the sampling team should be the guide in the selection of the most representative site.(6)

TABLE 5.1 PROCESS TESTING GUIDE^a (3)

Process	Test	Frequency
<u>PRETREATMENT</u>		
<u>Grit Removal</u>	Volatile Solids	Daily
	Total Solids	Daily
	Moisture Content	Daily
<u>PRIMARY TREATMENT</u>		
<u>Primary Sedimentation</u>	Settleable Solids	Daily
	pH	Daily
	Total Sulfides	Daily
	Biochemical Oxygen Demand	Weekly
	Suspended Solids	Weekly
	Chemical Oxygen Demand	Weekly
	Dissolved Oxygen	Weekly
	Grease	Weekly
<u>SECONDARY TREATMENT</u>		
<u>Activated Sludge</u>	Suspended Solids	Daily
	Dissolved Oxygen	Daily
	Volatile Suspended Solids	Weekly
	Turbidity	Daily
<u>Trickling Filter</u>	Suspended Solids	Daily
	Dissolved Oxygen	Daily
<u>Oxidation Ponds</u>	Dissolved Oxygen	Daily
	Total Sulfides	Daily
	Total Organic Carbon	Weekly
	Total Phosphorus	Weekly
	Settleable Solids	Daily
	pH	Daily
	Total Sulfides	Daily
<u>Final Sedimentation</u>	Biochemical Oxygen Demand	Weekly
	Suspended Solids	Weekly
	Chemical Oxygen Demand	Weekly
	Dissolved Oxygen	Weekly
	Turbidity	Daily
	MBAS	Weekly

^a This is a minimum sampling guide, and is subject to change with plant site, complexity of operation, and problems encountered.

(continued)

TABLE 5.1 (continued)

Process	Test	Frequency
<u>DISINFECTION</u>		
<u>Chlorination</u>	Chlorine Residual MPN Coliform	Daily Weekly
<u>SOLIDS HANDLING</u>		
<u>Thickening</u>	Suspended Solids Volatile Solids	Daily Daily
<u>Digestion</u>	Total Solids Volatile Solids pH Gas Analysis Alkalinity Volatile Acid	Weekly Weekly Daily Weekly Weekly Weekly
<u>Centrifuging</u>	Suspended Solids Volatile Solids	When in Operation When in Operation
<u>Vacuum Filters</u>	Sludge Filterability Suspended Solids Volatile Solids	When in Operation When in Operation When in Operation
<u>Incineration</u>	Ash Analysis	When in Operation
<u>ADVANCED TREATMENT</u>		
<u>Chemical Coagulation & Flocculation Activated Carbon</u>	Jar Test Phosphorus Analysis Apparent Density COD TOC	Weekly Weekly Weekly Weekly Weekly
<u>Recarbonation Ammonia Stripping Filters</u>	pH Ammonia Nitrogen pH Suspended Solids Turbidity	Weekly Weekly Weekly Daily Daily
<u>Microscreen</u>	Suspended Solids Chemical Oxygen Demand	Daily Weekly

TABLE 5.2 RECOMMENDED MINIMUM SAMPLING PROGRAMS FOR MUNICIPAL
WASTEWATER TREATMENT PROCESSES (4)

	Overall	Grit Removal	Primary-Clarification	Activated Sludge	Trickling Filter	Aerated Pond	Secondary Ponds	Secondary Clarifier	Chlorine Contact	Chemical Treatment	Nitrogen Removal	Two Stage Recarbon	Filtration	Activated Carbon	Centrifugation	Sludge Concentration	Solids Reduction	Aerobic Digestion	Solids Reduction	Anaerobic Digestion
	S ¹ F ²	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F
Temp	G 1/D						G 1/D	G 1/W				G 3/D							G 1/D	Mo
pH	G 1/D			G 5/W			G 3/W	G 1/W	G 1/D	G 1/D	G 1/D	G 3/D	Mo	Mo					G 1/D	C 1/D
BOD	C 2/W		C 2/W	C 2/W	C 2/W				C 2/W					G Back-wash		G 1/W	C 2/W	C Dump	G 1/D	
DO	G 3/W			G 5/W			G 1/D	G 1/W						G Back-wash		G 1/D	C 1/D	C 3/W		
SS	C 3/W		C 3/W	C 5/W					C 3/W	C 1/D				G Back-wash		G 1/D	C 1/D	C Dump	G 1/W	
NH ₃ -N	C 1/W			C 1/D					C 1/D			C 1/W								
TKN	C 1/W			C 1/D					C 1/W			C 1/W								
NO ₃ -N	C 1/W			C 1/D					C 1/D			C 1/W								
P-T	C 1/W			C 3/W					C 1/D		C 3/W									
Turb	R								Mo						R					
TS	C 2/W	G 2/W	G 1-3/W						G 3/W		G 1-3/W		C 1/W			G 1/D	G 1/D	C 2/W	C 1/W	
TVS	C 2/W	G 2/W		C 3/W														C 2/W	C 2/W	
Set. 5																				
Sl. Vol.			G 3/W						C 1/D							G 1/H		C 3/W		
COD				C 1/W	C 2/W	C 2/W				G 3/D				C 3/W						
V. SS				C 3/W																
Air Input						R														R

(continued)

TABLE 5.2 (continued)

	Overall	Grit Removal	Primary Clarification	Activated Sludge	Trickling Filter	Aerated Pond	Secondary Ponds	Secondary Clarifier	Chlorine Contact	Chemical Treatment	Nitrogen Removal	Two Stage Recarbon	Filtration	Activated Carbon	Centrifugation	Sludge Concentration	Solids Reduction	Aerobic Digestion	Solids Reduction	Anaerobic Digestion
	S ¹ F ²	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F	S F
Micro Analysis				G 2/W																
Ortho-P				C 3/W				C 1/D												
Chlor. Resid.									G 1/D		C 3/W									
Coliform									R											
Fecal Coliform									G 1/W											
Alk.	C 2/W							C 1/W	G 1/W	C 2/W		C 1/D						G 2/W	G 1/D	
Jar Test									C 1/W											
Hardness									C 1/W		C 1/W									
Sludge Vol.								G 3/D	C 1/W											
Dis. S	C 2/M			G 3/D							C 1/W									
MBAS											G 3/W	C 1/W								
Metals	C 2/M													C 1/D						
Plant Flow	R																			

1. S = type of sample
2. F = frequency

G = Grab
C = 24 hour composite
D = Day
W = Week

M = Month
R = Record continuously
Mo = Monitor continuously

5.4.1 Influent

Influent wastewaters are preferably sampled at points of highly turbulent flow in order to insure good mixing; however, in many instances the desired location is not accessible. Preferable raw waste sampling points are:(6)

- a. the upflow siphon following a comminutor (in absence of grit chamber)
- b. The upflow distribution box following pumping from main plant wet well
- c. aerated grit chamber
- d. flume throat
- e. pump wet well

In all cases, samples should be collected upstream from recirculated plant supernatant and sludges.

5.4.2 Effluent

Collect effluent samples at the most representative site downstream from all entering waste streams. When manually compositing effluent samples according to flow where no flow measuring device exists, use the influent flow measurement without any correction for time lag. The error in influent and effluent flow measurement is insignificant except in those cases where extremely large volumes of water are impounded, such as in reservoirs, as a result of influent surges coupled with highly restrictive effluent discharge.(7)

5.4.3 Pond Sampling

Composite samples from ponds with long detention times may not be representative because of the tendency of lagoons to short circuit. If dye studies or past experience indicate a homogeneous discharge, grab samples may be representative of the waste stream.

5.4.4 In-Plant Location

Apply the statistical technique outlined in Section 4.5 to determine in-plant sampling locations. In addition to these locations, sample all other unit processes periodically or when the variability of a parameter adversely affects the efficiency of a unit process.

5.5 NUMBER OF SAMPLES

Use one or more of the following methods to determine the number of samples:

1. Follow permit requirements by regulatory agencies.

2. Apply statistical methods in Section 4.2 to the data from the preliminary survey.
3. Use the frequency data to establish number of samples. For example, one sample every six hours will establish four samples per day.

5.6 PARAMETERS TO MEASURE

The NPDES permit for each municipal treatment plant dictates the effluent limitations and monitoring requirements for that particular plant. For evaluating the plant performance, regardless of the size, BOD₅, solids, pH and flow should be monitored routinely.(8)

Secondary analyses may include:

- | | |
|--------------------------|--|
| 1. Fecal Coliform | 8. Chlorine Residual |
| 2. Temperature | 9. Dissolved Solids |
| 3. Dissolved Oxygen | 10. Alkalinity |
| 4. Total Solids | 11. Metals |
| 5. Total Volatile Solids | 12. COD |
| 6. Nitrogen Series | 13. Oil and Grease |
| 7. Phosphorus | 14. Organic Priority Pollutants
as required |

Table 5.2 indicates the parameters to analyze the efficiency or the effectiveness of the various unit processes. Changes are allowed to compensate for specific plant conditions.

5.7 TYPE OF SAMPLE

Collect composite samples for overall monitoring,(6) and grab samples for checking individual unit processes. Use one of the following types of composite samples to properly estimate mass loading:

1. Periodic, time constant, sample volume proportional to stream flow.
2. Periodic, sample volume constant, time proportional to stream flow since the last sample.

Other composite types may be used if comparable results can be demonstrated.

5.8 METHODS OF SAMPLING

Choose manual or automatic sampling depending on how the advantages and disadvantages of the methods apply to the specific program. (Refer to Chapter 2). Only trained personnel should be entrusted the task of sample collection. Much of the uncertainty regarding the collection of suspended solids can be minimized if samples are collected at isokinetic conditions or

at higher intake velocities.

5.8.1 Automatic Sampler

Automatic samplers for municipal wastewaters must be capable of collecting representative suspended solids samples throughout the collection and treatment system. While sampler selection will depend on site conditions, the following guidelines are suggested:

1. For sampling raw wastewater and primary effluent, use a sampler having an intake velocity greater than 0.76. m/sec. (2.5 ft./sec.). For sampling a final effluent with no visible solids, a sampler having a lower intake velocity may be acceptable.(2)
2. To determine the effectiveness of an automatic sampler to collect suspended solids, statistically compare the suspended solids value of the composite sample from the automatic sampler with the mean value of the manual grab samples. The minimum compositing period should be six hours with a maximum individual sample frequency of one hour.(7) The ratio of the automatic sampler suspended solids value to the manual grab suspended solids value varies throughout the plant. For influent and primary effluent the acceptable ratio is 1.6 - 2.0 and for the final effluent it is 0.9 - 1.3.(9)

5.9 VOLUME OF SAMPLE AND CONTAINER TYPE

The volume of sample obtained should be sufficient to perform all the required analyses plus an additional amount to provide for any split samples or repeat examinations. Although the volume of sample required depends on the analyses to be performed, the amount required for a fairly complete analysis is normally 7.57 liters (two gallons) for each laboratory receiving a sample. The laboratory receiving the sample should be consulted for any specific volume requirements. Individual aliquot portions of a composite sample should be at least 100 milliliters (0.21 pints). Depending on the sampling frequency and sample volume, the total composited sample should be at least 7.57 liters (two gallons).(6) Use a separate sterilized container for coliform analysis. See Chapter 12 for trace organic collection methods. Collect chlorine residual and oil and grease samples in glass containers with teflon lined lids. Plastic is acceptable for the other inorganic and general organic analyses. Additional information for sampling organic parameters is given in Chapter 17.

5.10 PRESERVATION AND HANDLING THE SAMPLES

Follow the guidelines provided in Chapter 17 for the preservation and handling of samples.

5.11 FLOW MEASUREMENTS

The flow measurement technique selected should be in relation to the sampling location, type of flow, and other similar characteristics. Follow the guidelines enumerated in Chapter 3 on Flow Measurements. Primary and secondary flow measurement devices should be calibrated prior to taking flow measurements.

5.12 REFERENCES

1. Metcalf and Eddy, Inc. Wastewater Engineering. McGraw Hill, New York, 1972.
2. NPDES Compliance Sampling Manual. U.S. Environmental Protection Agency, Washington, D.C., June, 1977.
3. URS Research Co. Procedures for Evaluating Performance of Wastewater Treatment Plants. PB 228 849/6, National Technical Information Service, Springfield, Virginia.
4. Estimating Laboratory Needs for Municipal Wastewater Treatment Facilities. PB 227 321/7. National Technical Information Service, Springfield, Virginia.
5. Henderson, F.M. Open Channel Flow. MacMillan Co., New York, 1966.
6. Harris D.J. and W.J. Keefer. Wastewater Sampling Methodologies and Flow Measurement Techniques. EPA 907/9-74-005, U.S. Environmental Protection Agency, Region VII, 1974. 117 pp.
7. Barth, E.F. U.S. EPA Inter-Office Memo dated August 22, 1975.
8. Water Pollution Control Federation Highlights. Vol. 12 H-I, April, 1975.
9. Comparison of Manual (Grab) and Vacuum Type Automatic Sampling Techniques on an Individual and Composite Sample Basis. EPA-330/1-74-001, U.S. Environmental Protection Agency, Denver, Colorado, 1974. 29 pp.

CHAPTER 6

SAMPLING INDUSTRIAL WASTEWATERS

6.1 BACKGROUND

Industrial wastewaters vary significantly in pollution characteristics. This chapter presents general guidelines and considerations so that effective sampling programs can be established for varied situations.

6.2 OBJECTIVES OF SAMPLING PROGRAMS

6.2.1 Regulatory

Sampling of industrial wastewaters is required by regulatory agencies for the NPDES permit program. The location or sampling points, frequency and sample type are specified in the NPDES permit. At the time of NPDES permit modifications, incorporate the recommendations of Compliance Sampling Inspections.

6.2.2 Process Control

In addition, sampling is performed within the plant to monitor individual waste streams, as a check on the process efficiencies and to compute material balances.

6.2.3 Research and Development

The special needs of each research and development project on industrial waste treatment will dictate the sampling program. No general guidelines can be given. Projects are normally conducted:(1)

1. To explore potential recovery from a given department or unit process. Projects consider process modifications and study the economics of changes.
2. To define factors influencing character of wastes from a given department or unit process.
3. To investigate and demonstrate variations in the character and concentration of combined wastes.
4. To establish a sound basis for the treatment of residual wastes.

6.3 FREQUENCY OF SAMPLING

6.3.1 Established by Regulation

Use permit requirements when compliance monitoring is the objective. If the sampling frequency is not specified by regulation, sampling interval should be one hour or less, (2) and if data is available use the statistical methods as a tool to determine the frequency of sampling.

6.3.2 Use of Statistics

Apply the statistics outlined in Section 4.3, to obtain frequency of sampling whenever possible. Background data must be collected to determine mean and variance. One of the following procedures can be used to obtain this information (listed in order of preference) if it has not been previously collected:

1. Conduct a week long preliminary survey consisting of the hourly samples to characterize the system.
2. Conduct one 24 hour survey taking hourly samples (as outlined in Chapter 2). Analyze individual samples if batch dumps are suspected. Any weekly pattern must be considered and samples taken on the day of the greatest variation of the parameters of interest.
3. Obtain data from a plant with the same type of industrial operation. However, where processes differ, take samples to quantify the variation.

After data collection, use production figures to estimate extreme values, assuming a linear operating relationship (which is not always the case).

6.3.3 Other Considerations

Consider variable plant operations when determining frequency:

1. Seasonal operation
2. Less than 24 hour per day operation
3. Special times during the day, week or month set aside for cleanup
4. Any combination of the above

When monitoring these types of operations, it is necessary to sample during normal working shifts in the season of productive operation. Figure 6.1 gives procedures for the various situations.

6.4 LOCATION OF SAMPLING POINTS

6.4.1 Effluent Monitoring

Regulatory permits establish effluent monitoring points within a plant. The permit may specify only the total plant discharge or a specific discharge from a certain operation or operations. Consult permits for these

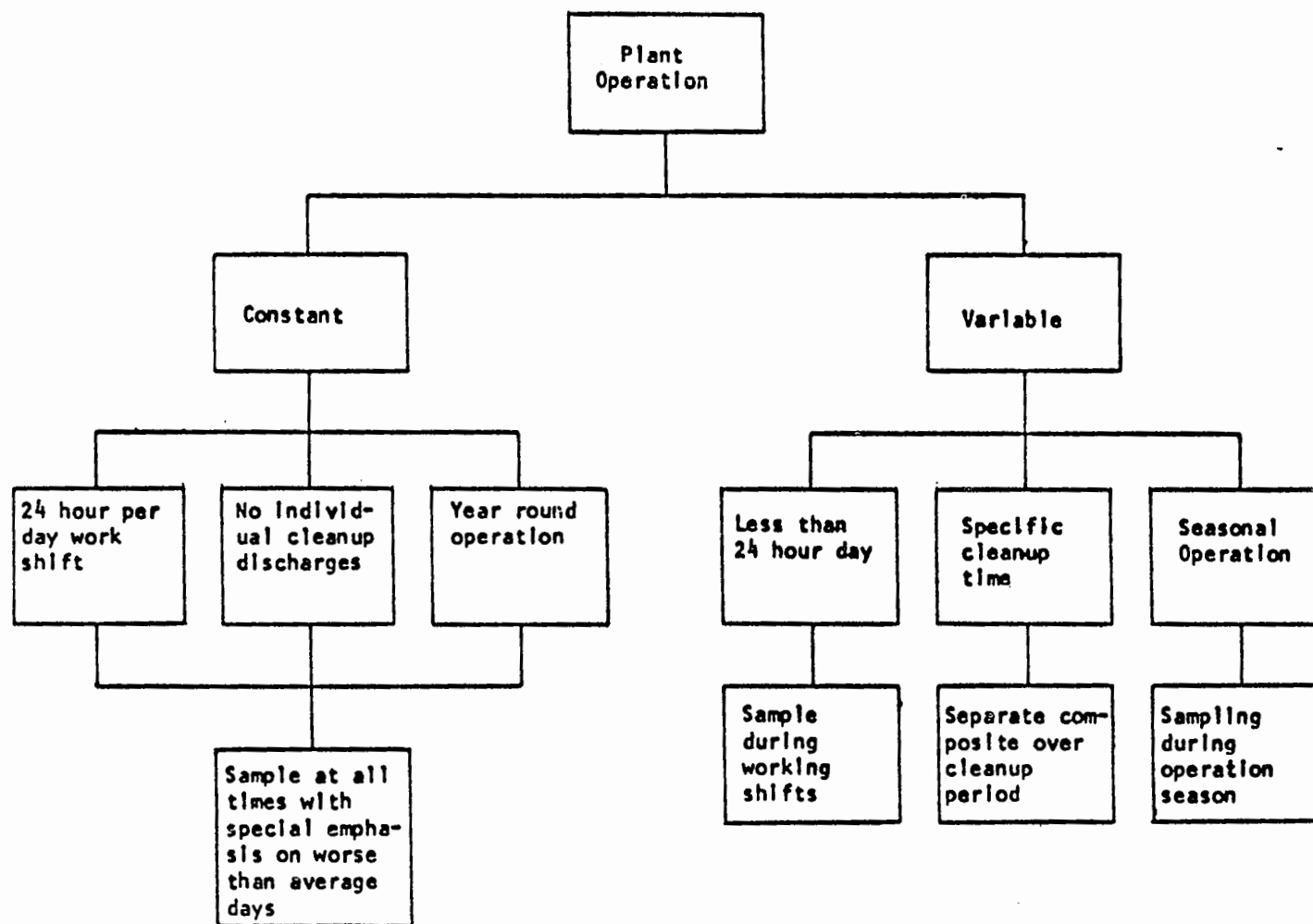


Figure 6.1 Factors of plant operation to be considered in the design of the sampling program. (2)

locations, or use those recommendations for obtaining representative samples given in Chapter 2.

6.4.2 In-Plant Locations

To achieve process control or to design and implement in-plant pollution control programs, selection of proper in-plant sample location is important. Use the following procedures to determine the sampling locations:

1. Become familiar with the plant processes and sources of wastes from unit operations.
2. Ascertain the sewer layout in the plant. If a sewer plan exists thoroughly review the sewer plan and examine each sewer to determine its course and destination. Where a sewer plan is not available, the only practical way to determine the sewer layout is by dye-tracing.
3. Determine the exact source and the point at which each waste stream enters the sewer.
4. Sample each waste stream and plant outfall. By doing so, each waste stream is characterized and the outfall characterizes the total plant effluent.
5. Sample each batch discharge.
6. If a point of upset exists within the plant, establishment of a sampling station or monitoring equipment at that point will allow early detection.
7. If data on different waste streams is available from past records, use statistical techniques outlined in Section 4.5.1 as an aid to establish the critical sampling locations within the plant.

6.5 NUMBER OF SAMPLES

Determine the number of samples from the following:

1. Follow NPDES permit requirements
2. Where NPDES permit is not applicable:
 - . Apply statistical methods (Section 4.2) to data from a preliminary survey.
 - . To effectively determine the concentration and types of pollutants discharged, collect no less than three operating day composite samples.(2)

6.6 PARAMETERS TO MEASURE

6.6.1 NPDES Requirements

Parameters required for measurement in NPDES permits are listed by industry in Table 6.1.(3) These are the parameters commonly required and are minimal guidelines where exact permit specifications do not exist.

TABLE 6.1 NPDES EFFLUENT LIMITATION PARAMETERS BY INDUSTRY

	Dairy Products	Grain Mills	Canned & Preserved Fruit & Veg.	Canned & Preserved Seafood	Sugar Products	Textiles	Cement	Feedlots	Electroplating	Organic Chemicals	Inorganic Chemicals	Plastics & Synthetics	Soap & Detergents	Fertilizer Mfg.	Petroleum Refining	Iron & Steel Mfg.	Non-Ferrous Metals	Phosphate Mfg.	Stationary Electric Power Generating Equip	Ferroalloy Mfg.	Leather Tanning and Finishing	Glass Manufacturing	Asbestos Mfg.	Rubber Products	Timber Products	Pulp, Paper, etc.	Bullders Paper & and Board	Meat Products	Printure Ink and Paint	Paving & Roofing Materials
Temperature Discharges	X				X		X																							
BOD - 5 Day	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Suspended Solids	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Oils, Fats & Grease	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Ammonia	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Nitrite-Nitrogen	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Nitrate-Nitrogen	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Nitrogen (Kjeldahl)	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Phosphorus	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Sulfite	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Sulfide	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Sulfate	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Chloride	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Chlorine	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Fecal Coliform Bact.	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Fluoride	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Berlin	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Boron	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Cadmium	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Chromium	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Cobalt	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Copper	X	X	X	X	X	X	X	X		X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

TABLE 6.1 (Continued)

	Dairy Products	Grain Mills	Canned & Preserved Fruit & Veg.	Canned & Preserved Seafood	Sugar Products	Textiles	Cement	Feedlots	Electroplating	Organic Chemicals	Inorganic Chemicals	Plastics & Synthetics	Soap & Detergents	Fertilizer Mfg.	Petroleum Refining	Iron & Steel Mfg.	Non-Ferrous Metals	Phosphate Mfg.	Stationary Electric Power Generating Equip	Farroalloy Mfg.	Leather Tanning and Finishing	Glass Manufacturing	Asbestos Mfg.	Rubber Products	Timber Products	Pulp, Paper, etc.	Builders Paper & Board	Heat Products	Printure Ink and Paint	Paving & Roofing Materials
Lead	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
pH																														
Manganese																														
Mercury																														
Nickel																														
Zinc																														
Phenols																														
PCBs																														
Aldrin																														
Dieldrin																														
Heptachlor																														
Color																														
COD																														
Cyanide																														
Iron																														
Surfactants																														
Aluminum																														
Arsenic																														
Settleable Solids																														

6.6.2 Other Parameters

Apply the techniques from Section 4.4 to establish parameters to measure. If process control is desired, measure the critical constituent. For example, if a distillation tower is to be controlled, monitoring the organic carbon content of the discharge stream may provide early information of leaks in the system.

6.7 TYPE OF SAMPLE

The permit will specify the type of sample, grab or composite, for effluent monitoring, but consider both types for in-plant monitoring. Where in-plant data do not exist, conduct a preliminary survey with production personnel of each unit process to determine the chemical reactions, production variability, location of individual waste streams and their potential variability, and potential chemical constituents in each waste stream. After careful analysis of the unit process, select the appropriate type of sample to be collected. Collect proportional composite samples to determine the average amount of pollutant or collect grab samples:

1. If a batch discharge is to be characterized.
2. If the flow is homogeneous and continuous with relatively constant waste characteristics so a grab sample is representative of the stream.
3. When the extremes of flow and quality characteristics are needed.
4. When one is sampling for a parameter requiring that the entire sample be used for analysis with no interior transfers of containers, for example, oil and grease.
5. When sampling for parameters which change character rapidly such as dissolved gases or those which cannot be held for a long length of time before analyses, for example, bacteria counts, chlorine, dissolved oxygen and sulfide.

6.8 METHOD OF SAMPLING

Choose manual or automatic sampling depending upon which method is best for the specific sampling program. (Refer to Chapter 2). Only trained personnel should be entrusted the task of sample collection.

6.8.1 Automatic Samplers

If an automatic sampler is to be used, the actual type of sampler is determined by the constituents in the wastewater. A list of samplers and their features are given in Table 2.3. The features and techniques for use of automatic samplers are discussed in Section 2.3.2. To choose a sampler, list the features needed for sampling the type of industrial wastewater, as outlined in Section 2.3.2.3. If the variability of the wastewater is not

known or is large, use a sampler containing a multiplex feature, which permits the collection of a composite sample in a single container while collecting one or several discrete samples during a preset time interval. Once the needed features have been established, the sampler which best matches these features can be selected. Available samplers may need adaptation. It is imperative that the stream be well mixed at the sampling point to avoid problems when using automatic samplers in streams with a high solids content.

6.9 VOLUME OF SAMPLE AND CONTAINER TYPE

The volume of sample to be taken is determined by the number of analyses to be performed on the sample. If this has not been determined, a grab sample volume, a minimum of 7.57L (2 gallon) and an individual composite volume of 100 milliliters (0.21 pints) should be taken. The container type is also contingent upon the analysis to be run.

6.10 PRESERVATION AND HANDLING OF SAMPLES

The preservation, holding times, and materials associated with sampling depends upon the parameters to be analyzed. Guidance submitted for approval to the 304 h committee, U.S. Environmental Protection Agency, is shown in Chapter 17. Because approval and subsequent publication in the Federal Register has not taken place as of publication of this Handbook, the reader is urged to keep abreast of future changes through Federal Register publications.

6.11 FLOW MEASUREMENT

Flow measurement techniques adopted should be in relation to the sampling location, type of flow, and other similar characteristics. Refer to Chapter 3 on Flow Measurements. Primary and secondary devices should be calibrated prior to taking flow measurements.

6.12 REFERENCES

1. Black, H.H. Procedure for Sampling and Measuring Industrial Waters. Sewage Industrial Wastes. 24:45, January, 1952.
2. Rabosky, J.G. and D.L. Koraido. Gaging and Sampling Industrial Wastewaters. Chemical Engineering 80 p. 111-120, January 8, 1973.
3. N.F.I. C-Denver. Effluent Limitations Guidelines for Existing Sources and Standards of Performance for New Sources for 28 Point Source Categories. Denver, Colorado, p. 122, August, 1974.

CHAPTER 7

SAMPLING AGRICULTURAL DISCHARGES

7.1 BACKGROUND

Agricultural discharges can be separated into three types: concentrated animal waste or manure from a confined feedlot, run-off from an agricultural watershed, and irrigation return flow. These three types of run-off differ mainly in the concentration of pollutants. Field run-off from rainfall, irrigation and snowmelt is characteristically the least polluted, while feedlot run-off is the most concentrated waste. The concentrations of pollutants from field run-off and irrigation return flow vary with the amount and intensity of rainfall or snowmelt, irrigation practices, land use, topography, soil type and use of manure or fertilizer.

7.2 OBJECTIVES

Agricultural discharges are sampled to study both field and feedlot run-off, or to monitor field or treated feedlot run-off for regulation.

7.3 FREQUENCY OF SAMPLING

7.3.1 Feedlot Discharge

7.3.1.1 Regulatory

The sampling frequency must follow that given in the discharge permit. Daily sampling is the maximum requirement in most permits.

7.3.1.2 Other

Apply the spectral analysis techniques as outlined in Section 4.3.1. Collect preliminary data if not available by conducting one of the following (in order of preference)

- a. A one week survey collecting hourly grab samples where the discharge is continuous.
- b. A 24-hour survey collecting hourly grab samples.

Calculate the mean and variance as indicated in Sections 4.1.1.1 and 4.1.1.4 and apply a computer program for spectral analysis.

7.3.2 Field Run-off and Irrigation Return Flow

Apply the statistical methods outlined in Section 4. If possible, collect preliminary data by sampling every five minutes for the duration of several run-off events.(1) Collect and analyze samples individually or composite them proportional to flow, depending on the objectives of the study. Since most of the variability in the run-off occurs during the initial part of the run-off hydrograph on the rising side of flow crests, sampling is the most critical at this time.

7.4 LOCATION OF SAMPLING POINTS

7.4.1 Feedlot Discharge

Channel feedlot run-off to a central point by sloping or trenching if no treatment is provided. If treatment is provided, sample effluent from the treatment system.

7.4.2 Field Run-off and Irrigation Return Flow

Select a site downstream of the run-off area at a point where run-off collects into a channelized flow. Use the topography of the area to locate this point. Choose a location with sufficient depth to cover the sampler intake without excavation. Irrigation tailwater should be sampled and measured quantitatively at the lower end of the field before it comesles with other waters in the drainage ways.

7.5 NUMBER OF SAMPLES

The number of samples for both feedlot discharge and field run-off are determined by 1) Following regulatory requirements, and 2) Applying the statistics in Section 4 after the mean and variance are determined through a preliminary survey (see Section 7.3).

7.6 PARAMETERS TO ANALYZE

7.6.1 Established by Regulation

Analyze all parameters required by discharge permits.

7.6.2 No Requirements

Analyze for (2,3,4,5,6), Nutrients (total phosphate and nitrogen series), Demand (BOD,COD,TOD), Physical/Mineral (total and suspended solids), fecal coliform and fecal streptococci, Total Dissolved Solids, and other analyses such as metals, pesticides, or herbicides.

7.7 TYPE OF SAMPLE

Do not collect a single grab sample due to the high variability of run-off. Collect a series of samples for analyses, or form a composite sample according to flow using one of the methods described in Section 2.4.5.

7.8 METHOD OF SAMPLING

Collect samples automatically or manually. Collect discrete samples separately or composite them proportional to flow. For sampling field run-off, use an automatic system activated by run-off through the flume. Typical sampling/flow measurement stations are shown in Figures 7.1 and 7.2. If feedlot run-off contains large particulate matter such as corn cobs, manual sampling will be necessary.

7.9 VOLUME OF SAMPLE AND CONTAINER TYPE

Use multiple containers for samples to provide the best preservation for specific parameters. For example, if the parameters given in Section 7.6.2 (nutrients, demand, physical/mineral, microbiological) are to be analyzed, three containers and three preservation techniques would be required for each sample.

<u>Container</u>	<u>Parameter Group</u>	<u>Technique</u>
1	Nutrients	Add H_2SO_4 to pH 2 or 40-400 mg/l HgCl_2 and refrigerate at 4°C
2	Demand, TDS (Physical/Mineral)	Ice as soon as possible after collection
3	Microbiological	Collect grab sample in sterile container and ice as soon as possible, hold for no longer than six hours

7.10 FLOW MEASUREMENT

Select the flow measurement device based on the specific application and the necessary degree of accuracy. A type H flume is advantageous because of its wide range of accuracy.(3)(7) Instrumentation should include a continuously recording flow chart, with a pressure-sensitive record preferred to ink. A schematic of a typical installation is shown in Figure 7.3. More detailed information on flow measurement is given in Chapter 3.

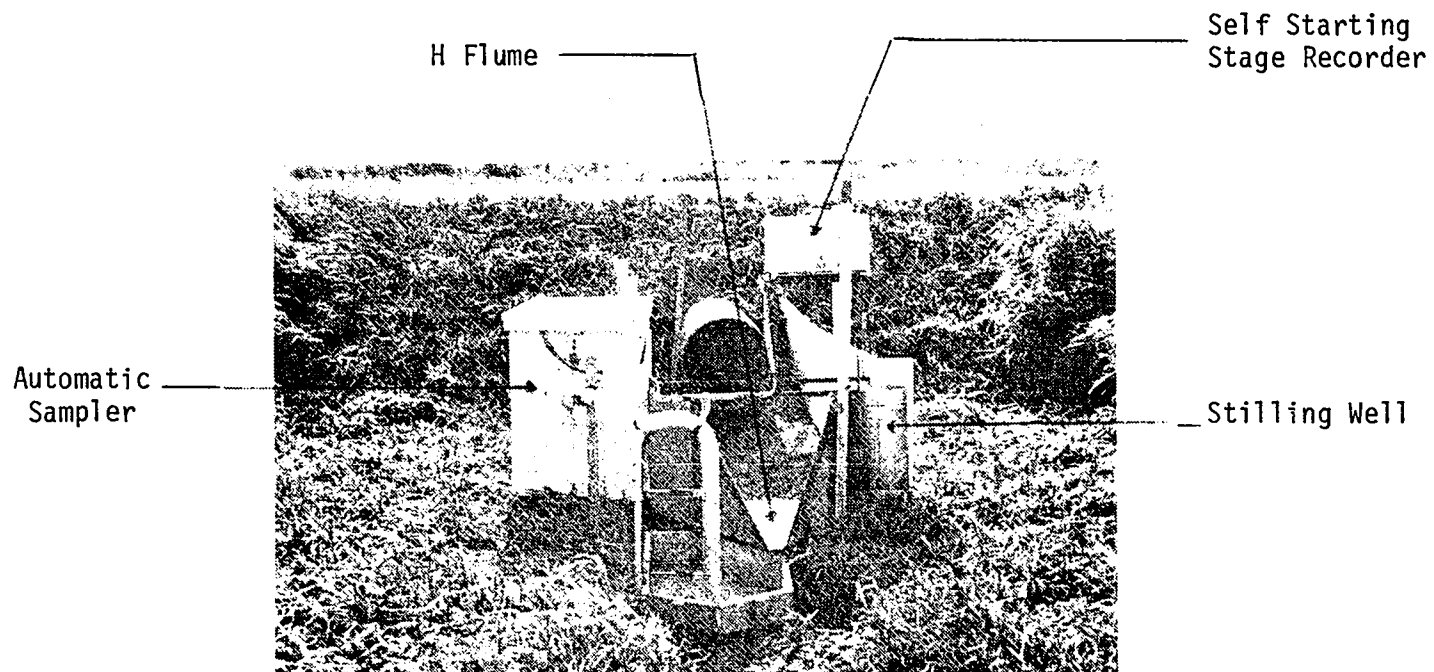


Figure 7.1 View of field installation (from 8)

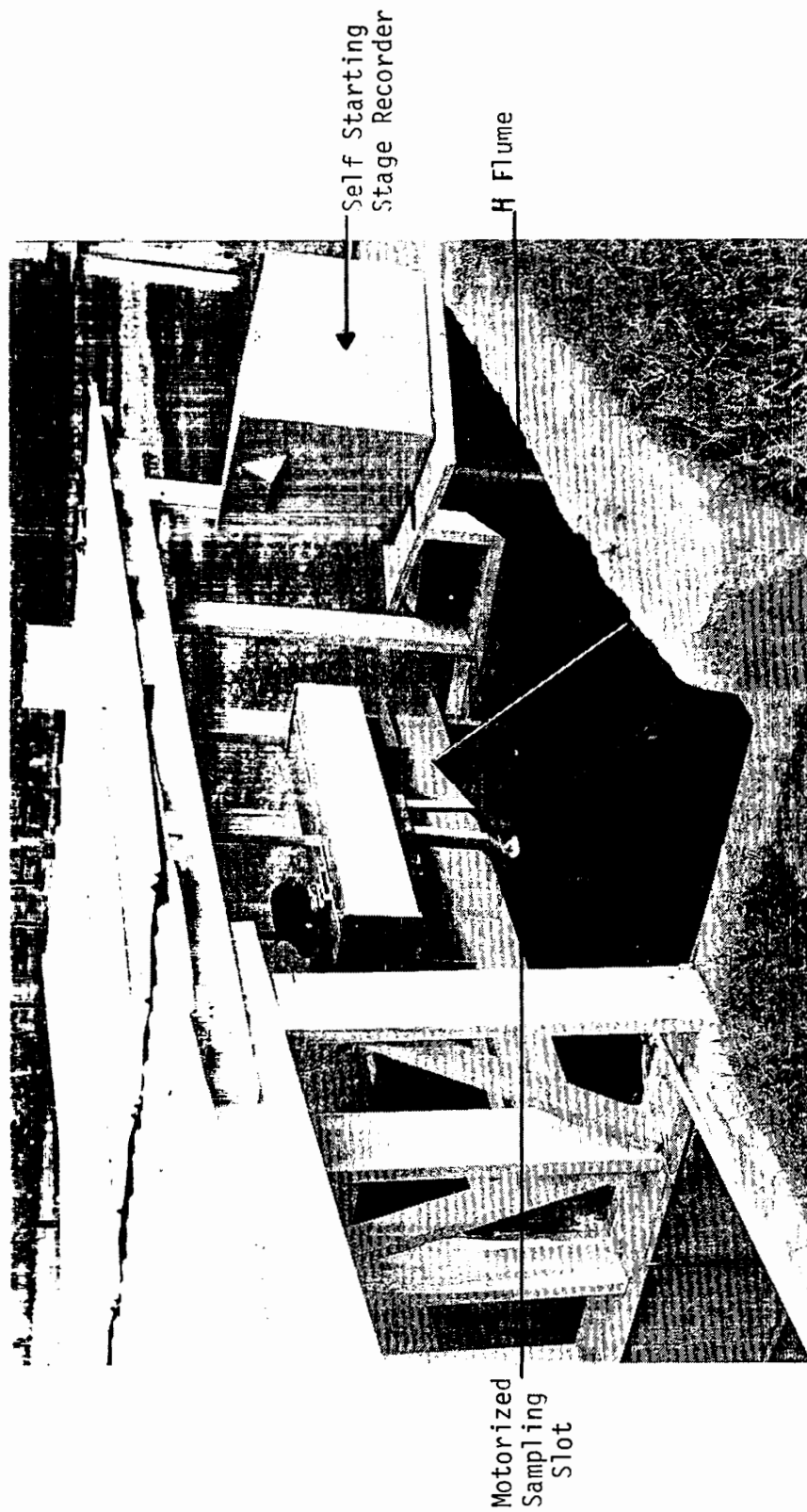


Figure 7.2 View of field installation (9)

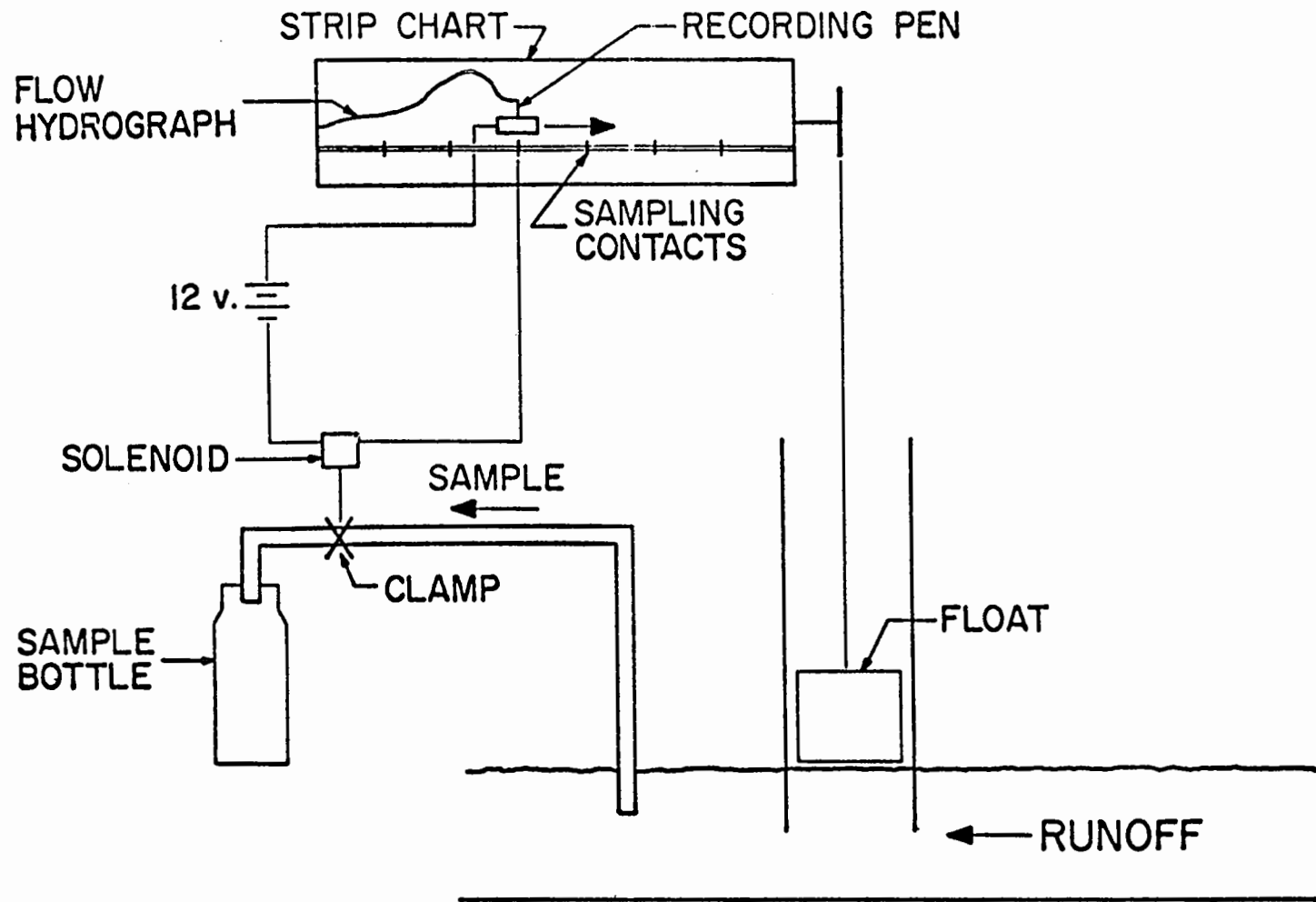


Figure 7.3 Schematic of water level recorder and sampler arrangement (from 8)

7.11 REFERENCES

1. Miner, J.R., L.R. Bernard, L.R. Fina, G.H. Larson, and R.I. Lipper. Cattle Feedlot Runoff Nature and Behavior. Journal WPCF. 38: 834-847, October, 1966.
2. Humenik, F.J. Swine Waste Characterization and Evaluation of Animal Waste Treatment Alternatives. Water Resources Research Inst., Univ. of North Carolina, Raleigh, North Carolina, June, 1972. 152 p.
3. Harms, L.L., J.N. Dornbush and J.R. Anderson. Physical and Chemical Quality of Agricultural Runoff. Journal WPCF. 46: 2460-2470, November, 1974.
4. Robbins, J.W.D., D.W. Howells and G.J. Kriz. Stream Pollution from Animal Production Units. Journal WPCF. 44: 1536-1544, August, 1972.
5. Fitzsimmons, D.W., C.E. Braceway, J.R. Busch, L.R. Conklin and R.B. Long. Evaluation of Measures for Controlling Sediment and Nutrient Losses from Irrigated Areas. EPA-600/2-78-138, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, July, 1978.
6. Skogerboe, G.W., W.R. Walker and R.G. Evans. Environmental Planning Manual for Salinity Management in Irrigated Agriculture. EPA-600/2-79-062, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, March, 1979.
7. Madden, J.M. and J.N. Dornbush. Measurement of Runoff and Runoff Carried Waste from Commercial Feedlots. Proc. Int. Symposium on Livestock Wastes. Ohio State Univ., Columbus, Ohio. April 19-22, 1971. 44-47
8. Harms, L.L. South Dakota School of Mines and Technology. Rapid City, South Dakota. Personal Communication to Environmental Sciences Division. December 20, 1974.
9. Leonard, R.A., C.N. Smith, G.W. Langdale and G.W. Bailey. Transport of Agricultural Chemicals from Small Upland Piedmont Watersheds. Environmental Research Laboratory, Office of Research and Development, Athens, Georgia, EPA-600/3-78-056, May, 1978.

CHAPTER 8

SAMPLING SURFACE WATERS, AQUATIC ORGANISMS, AND BOTTOM SEDIMENTS

8.1 BACKGROUND

The sampling of rivers and streams, lakes and aquatic organisms, and their associated bottom sediments are considered in this chapter. For a more detailed discussion on aquatic sampling, consult the EPA biological methods manual.(1) The decisions regarding analytical parameters must be made at the beginning of the study in order to develop a rational sampling program.

8.2 OBJECTIVES OF THE STUDY

The main objectives of sampling surface waters, aquatic organisms, and sediments are:

1. Evaluation of the standing crop, community structure, species diversity, productivity and stability of aquatic organisms.
2. Evaluation of the quality and trophic state of a water system.
3. Determination of the effect of a specific discharge on a certain water body.

8.3 PARAMETERS TO ANALYZE

Surface waters and sediments are commonly analyzed for the chemical and biological parameters listed in Table 8.1.

8.4 LOCATION OF SAMPLING POINTS

Select the study site based on the program objectives, the parameters of interest, and the type of sample. For example, the following guidelines are suggested in the EPA Model State Water Monitoring Program (2) for selecting long term biological trend monitoring stations:

1. At key locations in water bodies which are of critical value for sensitive uses such as domestic water supply, recreation, propagation, and maintenance of fish and wildlife.

TABLE 8.1 COMMON MEASUREMENTS FOR SURFACE WATER, AQUATIC ORGANISMS
AND SEDIMENT SAMPLING

Chemical	Physical	Biological
Dissolved oxygen	Color	Fish
Phosphate	Turbidity	Benthic Macroin-vertebrates
Nitrogen series	Water temperature	Periphyton
Alkalinity	Stream velocity	Phytoplankton
Silica	Water depth	Zooplankton
pH	Sediment composition	Macrophytes
Specific Conductance		Macroalgae
Solids (TDS, TS, TSS)		Bacteria
Organic matter and demand		
Pesticides		
Heavy Metals		

2. In the main stream upstream and downstream from the confluence of major tributaries and in the tributary upstream from the confluence with the main stream.
3. Near the mouths of major rivers where they enter an estuary.
4. At locations in major water bodies potentially subject to inputs of contaminants from areas of concentrated urban, industrial, or agricultural use.
5. At key locations in water bodies largely unaffected by man's activities.

Use one of the following random or non-random sampling plans to determine sampling points within the study site. Sample selection is discussed in more detail in the EPA biological methods manual.(1)

8.4.1 Simple Random Sampling

Use a simple random sampling plan when there is no reason to subdivide the population from which the sample is drawn. Draw the sample such that every unit of the population has an equal chance of being selected. First, number the universe or entire set of sampling units from which the sample will be selected. This number is N. Then from a table of random numbers select as many random numbers, n, as there will be sampling units selected for the sample. Select a starting point in the table and read the numbers consecutively in any direction (across, diagonal, down, up). Determine the number of observations, n (sample size), prior to sampling. For example, if n is a two digit number, select two digit numbers ignoring any number greater than n or any number that has already been selected. Select these as the sampling units.

8.4.2 Stratified Random Sampling

Use a stratified random sampling plan if any knowledge of the expected size or variation of the observations is available. To maximize precision, construct the strata such that the observations are most alike within strata and most different among strata, in order to subtain minimum variance within strata and maximum variance among strata. Perhaps the most profitable means of obtaining information for stratification is through a prestudy reconnaissance or pilot study. For information on conducting a pilot study, consult the EPA biological methods manual.(1) Stratification is often based upon depth, bottom type, isotherms, or other variables suspected of being correlated with the parameter of interest. Select as many strata as can be handled in the study. In practice, however, gains in efficiency due to stratification usually become negligible after only a few divisions unless the characteristic used as the basis of stratification is very highly correlated with the parameter of interest.(2)

8.4.3 Systematic Random Sampling

Use a systematic random sampling plan to assure an adequate cross section while maintaining relative ease of sampling. A common method of systematic sampling involves the use of transect (Figures 8.1) or grid (Figure 8.2). However, choose a random starting point along the transect or grid to introduce the randomness needed to guarantee freedom from bias and allow statistical inference.

8.4.4 Nonrandom Sampling

Use a nonrandom sampling plan if justified by the study site, or parameters of interest, or the type of study being undertaken. For example, the following sample locations might satisfy the program objectives:

<u>Parameter</u>	<u>Sampling Location</u>
Fish	Shoreline sampling
Benthic macroinvertebrates	Right, left bank, midstream or transect
Periphyton	Shoreline sampling
Phytoplankton	Transect or grid
Zooplankton	Transect or grid
Macrophytes	Shoreline sampling or transect
Chemical	Transect or grid

8.4.4.1 Impact of Point Discharges

Use transect sampling scheme to determine the impact of a point discharge. A presurvey is recommended to determine the zone of influence.

1. Place lines transecting the receiving water at various angles from the discharge point.
2. Choose sampling intervals randomly or uniformly or by the methods described in Section 8.4.4.2.

3. Choose one or two remote control points to use as background.
4. See Figure 8.1 for example.

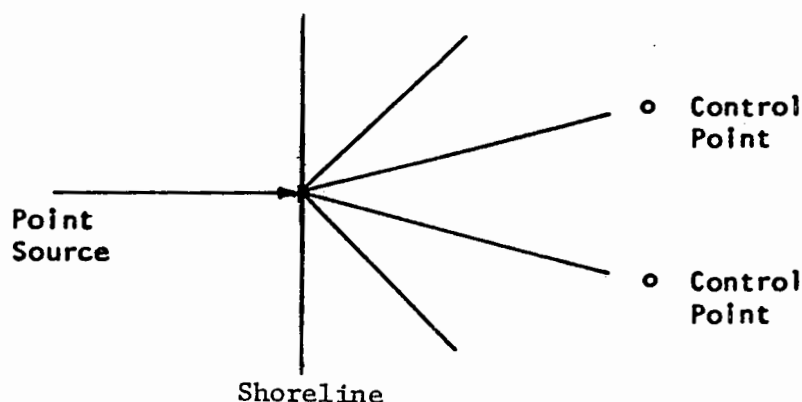


Figure 8.1 Example of transect sampling scheme in reservoirs, lakes and coastal waters

A grid sampling scheme may be used for some biological parameters. The grid must fit in a single environment, such as all riffles or all pools for a valid comparison.

1. Set up grids across and through the area to be sampled (that is, in both width and depth directions versus length) as required by the program.
2. The grid size is dependent upon the degree of lateral and vertical mixing. If the amount of mixing is unknown, then take a larger number of samples across and through the stream than would be otherwise desirable.
3. Choose the number of samples randomly, uniformly or using the procedure in Section 8.4.4.2.
4. Choose a control point upstream of the grid system and point source.
5. See Figure 8.2 for an illustration of the grid method.

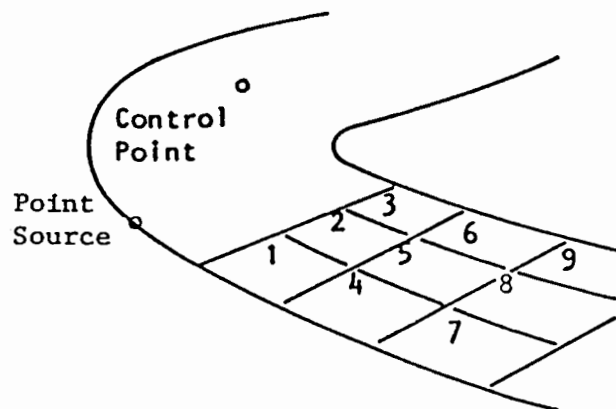


Figure 8.2 Example of grid sampling scheme in rivers

8.4.4.2 Spatial Gradient Technique

This technique may be used for the rational selection of sampling station locations.(3)(4) It presupposes the existence of historical data or some reasonable estimate of the expected variability of the parameters to be monitored over the region of interest, say, along the length of the river. This technique has greater applicability for chemical than biological parameters.

1. Collect historical or comparable data to estimate the mean and variance of the parameter of interest, Y .
2. Plot the maximum and minimum values of the parameter concentration versus distance along the river (Figure 8.3).
3. Calculate a slope for both lines (G_{\max} and G_{\min}).
4. Determine the difference between the slopes, i.e., $G_{\max} - G_{\min}$.
5. Determine the maximum allowable error in the estimates of the parameter value at Point B.
6.
$$d_{\max} = \frac{Y_{\max}}{G_{\max} - G_{\min}}$$
7. Use this d to determine distance between points on a transect or grid in a grid pattern.

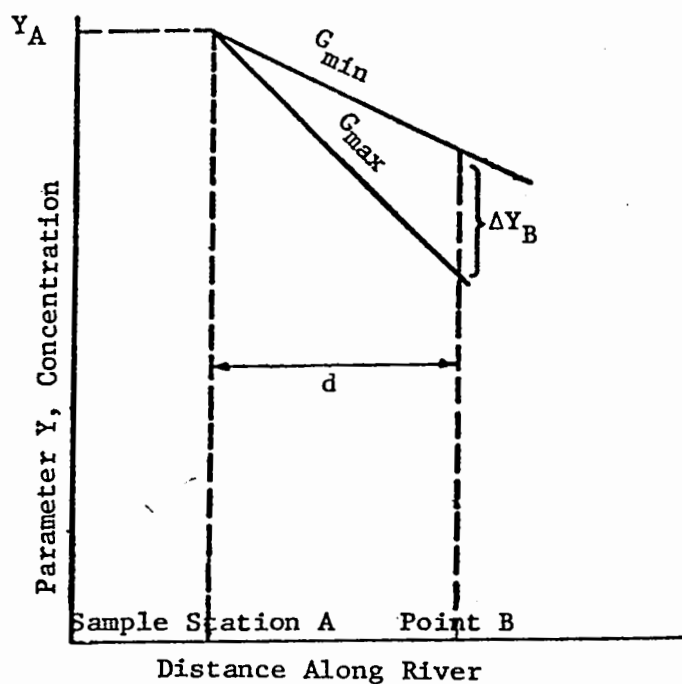


Figure 8.3 Use of spatial gradient technique for maximum spacing of sampling stations

8.5 RANDOM SAMPLING

The following information is summarized from the EPA biological methods manual.(1)

8.5.1 Simple Random Sampling

Use one of the following two methods depending on the decision variable.

1. Estimation of a Binomial Proportion - An estimate of the proportion of occurrence of the two categories must be available. If the categories are presence and absence, the probability of observing a presence is P ($0 < P < 1$) and the probability of observing and absence is Q ($0 < Q < 1$, $P + Q = 1$). The second type of

information which is needed is an acceptable magnitude of error, d , in estimating P (and hence Q). With this information, together with the size, n , of the population, the formula for n as an initial approximation (n_0), is:

$$n_0 = \frac{t^2 PQ}{d^2}$$

- a. For $n_0 > 30$, use $t = 2$. This n_0 ensures with a 0.95 probability that P is within d of its true value.
- b. For $n_0 < 30$, use a second calculation where t is obtained from a table of "Student's t " with $n_0 - 1$ degrees of freedom. If the calculation results in an n_0 , where

$$\frac{n_0}{N} < 0.05$$

no further calculation is warranted. Use n_0 as the sample size. If $\frac{n_0}{N} > 0.05$ make the following computation:

$$n = \frac{n_0}{1 + \frac{n_0}{N} - 1}$$

2. Estimation of a Population Mean for Measurement Data - In this case

as estimate of the variance S^2 , must be obtained from some source, and a statement of the margin of error, d , must be expressed in the same units as are the sample observations.

- a. For $n_0 > 30$, use
$$n_0 = \frac{t^2 s^2}{d^2}$$
- b. For $n_0 < 30$, recalculate using t from the tables, and if $\frac{n_0}{N} > 0.05$

$$n = \frac{n_0}{1 + \frac{n_0}{N} - 1}$$

After a sample size, n , is obtained from the population, the basic sample statistics may be calculated. If the sample size, n , is greater than 5% of the population ($\frac{n}{N} > 0.05$), a

correction factor is used so that the calculation for the sample variance is:

$$s^2 = \frac{N-n}{N} \frac{\sum X_1^2 - \frac{(\sum X_1)^2}{n}}{n-1}$$

8.5.2 Stratified Random Sampling

Conduct a pilot study or obtain reliable estimates of the variance within strata from other sources. If historical data have been collected, use optimal allocation to determine the total number of samples.

$$n = \frac{\frac{t^2 (\sum N_k s_k)^2}{N^2 d^2}}{1 + \frac{t^2 \sum N_k s_k^2}{N^2 d^2}}$$

Where t = Student's t value (use 2 for estimate)

N_k = number of sampling units in stratum k

s_k^2 = variance of stratum k

$s_k = \sqrt{s_k^2}$ = standard deviation of stratum k

N = total number of sampling units in all strata

d = acceptable parameter error

If no data are available, use proportional allocation to determine the total number of samples:

$$n = \frac{\frac{t^2 \sum N_k s_k^2}{N d^2}}{1 + \frac{\sum N_k s_k^2}{N^2 d^2}}$$

Use the following equations to determine the number of samples to be collected in each stratum, n_k :

$$\text{Optimal allocation: } n_k = \frac{n N_k s_k}{\sum N_k s_k}$$

Proportional allocation: $n_k = \frac{nN_k}{N}$

8.5.3 Systematic Random Sampling

Determine the number of samples to be taken on the grid or transect using the methods given in Section 8.4.4.2 or 8.5.1.

8.6 FREQUENCY OF SAMPLING

While the frequency of sampling will often be determined by the program, use the Model State Water Monitoring Program (1) guidelines for guidance in trend monitoring (Table 8.2).

8.7 METHOD OF SAMPLING

While compositing of individual grab samples is permitted for most chemical parameters, as a rule biological samples are not composited. For biological parameters, collect single grab samples.

8.8 TYPES OF SAMPLES FOR AQUATIC ORGANISMS

Choose the type of sampler that meets the needs of the sampling program by considering the advantages and disadvantages of the sampler type. In general, equipment of simple construction is preferred due to ease of operation and maintenance plus lower expense. Advantages and disadvantages of various water bottles are shown in Table 8.3 and illustrated in Figure 8.4. This equipment is useful for chemical, phytoplankton and zooplankton sampling. Corers and bottom grabs (Tables 8.4 and 8.5 and Figures 8.5 and 8.6) are useful for sediment sampling. Nets and substrate samplers are covered in Tables 8.6 and 8.7 and Figures 8.7 and 8.8.

There are inherent advantages of using a diver for sediment sampling. The diver can ascertain what is a representative sample in addition to taking pictures and determining qualitatively the current velocity.

8.9 VOLUME OF SAMPLE AND CONTAINER TYPE

Refer to Chapter 17 for specific information relative to the chemical parameters which are to be analyzed. In general, do not use metal samplers for trace metal nor use plastics for sampling trace organics. Refer to the biological methods manual (1) for container type and sample volumes, where applicable.

TABLE 8.2 MODEL STATE WATER MONITORING PROGRAM GUIDELINES FOR BIOLOGICAL MONITORING (1)

Community	Parameter	Priority ^a	Collection & analysis method ^b	Sampling frequency ^c
Plankton	Counts and identification Chlorophyll a; Biomass as ash-free weight	1	Grab samples	Once each; in spring, summer and fall
Periphyton	Counts and identification Chlorophyll a; Biomass as ash-free weight	1 2 2	Artificial substrate	Minimally once annually during periods of peak periphyton population density and/or diversity
Macrophyton	Areal coverage; Identification; Biomass as ash-free weight	2 2 2	As circumstances prescribe	Minimally once annually during periods of peak macrophyton population density and/or diversity
Macroinvertebrate	Counts and identification Biomass as ash-free weight Flesh tainting; Toxic substances in tissue ^d	1 2 2	Artificial and natural substrates	Once annually during periods of peak macroinvertebrate population density and/or diversity
Fish	Toxic substances in tissue ^d Counts and identification Biomass as wet weight; Condition factor; Flesh tainting Age and growth	1 2 2 2 2	Electrofishing or netting	Once annually during spawning runs or other times of peak fish population density and/or diversity

a Priority: 1) Minimum program; 2) Add as soon as capability can be developed.

b See EPA Biological Methods Manual.

c Keyed to dynamics of community.

d See "Analysis of Pesticide Residues in Human and Environmental Samples," USEPA, Perrine Primate Research Lab, Perrine, FL 32157 (1970), & "Pesticide Analytical Manual," USDHEW, FHA, Wash, D.C.

TABLE 8.3 COMPARISON OF WATER SAMPLERS

Device	Application	Material Contacted	Advantages	Disadvantages
Nansen Bottle	Phytoplankton	Teflon lined	Able to use in series	Small volume
Kemmerer Bottle	Chemical*	PVC	No metal contamination	Fixed capacity from 0.4-16 L
Van Dorn Bottle	Bacteriological Zooplankton	Brass Acrylic plastic	No metal contamination	Metal toxicity
	Chemical*	PVC	No metal contamination	Fixed capacity from 2-30 L
	Bacteriological Zooplankton Phytoplankton		No metal contamination	
Simple Bottle	Chemical* Bacteriological	Glass	Inexpensive	No depth control
Pumps	Chemical* Zooplankton Phytoplankton	430 Stainless Steel	Large volume, samples a vertical water column, continuous sample	Possible metal contamination, physical damage to organisms

* Organic chemicals such as pesticides, priority pollutants, etc. should be sampled with materials type such as teflon, glass, or other proven non-contaminating materials.

TABLE 8.4 COMPARISON OF BOTTOM GRABS/SAMPLERS

Device	Advantages	Disadvantages
Ponar	Safe, easy to use, prevents escape of material with end plates, reduces shock wave, combines advantages of others, preferred grab in most cases	Can become buried in soft sediments
Ekman	Use in soft sediments and calm waters, collects standard size sample (quantitative), reduces shock wave	Not useful in rough water; not useful if vegetation on bottom
Tall Ekman	Does not lose sediment over top; use in soft sediments and calm water, standard sample size, reduces shock wave	Not useful in rough waters, others as for Ekman
Peterson	Quantitative samples in fine sediments, good for hard bottoms and sturdy and simple construction	May lose sampled material, premature tripping, not easy to close; does not sample constant areas; limited sampling capacity
Smith-Mcintyre	Useful in bad weather, reduces premature tripping, use in depths up to 1500 m (3500 ft), flange on jaws reduces material loss, screen reduces shock waves, good in all sediment types	Large, complicated and heavy, hazardous for samples to 7 cm depth only, shock wave created
Diver	Can determine most representative sampling point and current velocity	Requires costly equipment and special training

TABLE 8.5 COMPARISON OF CORING DEVICES

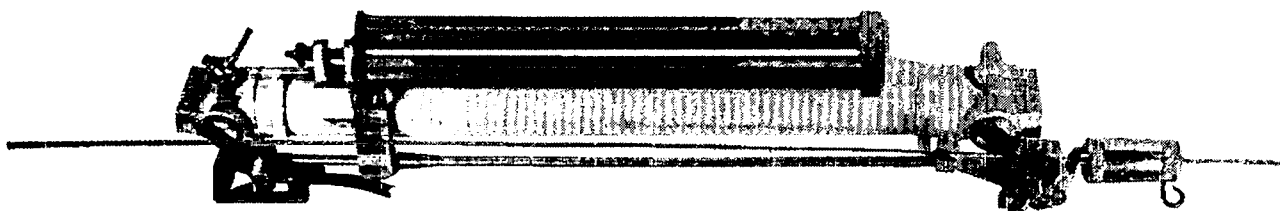
Device	Advantages	Disadvantages
Kajak or K.B. Corer	Does not impede free flow of water, no pressure wave, easily applied to large area	
Moore (Pfleger)	Valve allows sample to be held	Careful handling necessary to avoid sediment rejection, not in soft sediments
O'Conner	Can sample water with hard bottoms	Not in deep water
Elgmork's	Sample easily removed, good in soft muds, easy to collect, easy to remove sample	Not in hard sediments
Jenkins	Good in soft sediments and for collecting an undisturbed sediment-water interface sample. Visual examination of benthic algal growth and rough estimates of mixing near the interface after storms can be made	Complicated
Enequist	Good in soft/medium sediments, closing mechanism	Does not penetrate hard bottom
Kirpicenko	Soft and hard bottoms, various sizes, closes automatically	Not for stony bottoms

TABLE 8.6 COMPARISON OF NET SAMPLING DEVICES

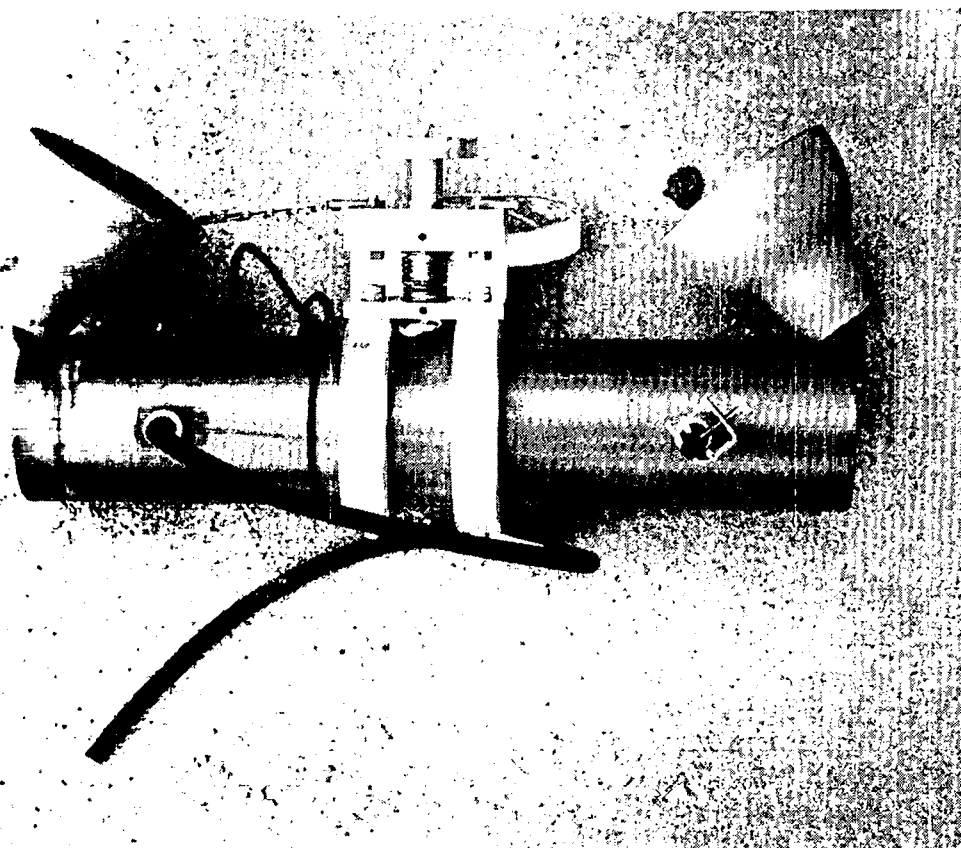
Devices	Application	Advantages	Disadvantages
Wisconsin Net	Zooplankton	Efficient shape concentrates sample	Qualitative
Clarke-Bumpus	Zooplankton	Quantitative	No point sampling, difficult to mea- sure accurately depth of sample

TABLE 8.7 COMPARISON OF SUBSTRATE SAMPLERS

Type of Substrate	Advantages	Disadvantages
1. <u>Artificial</u>		
Modified Hester-Dendy	Reduces compounding effects of substrate differences, multiplate sampler	Long exposure time, difficult to anchor, easily vandalized
Fullner	Wider variety of organisms	Same as modified Hester-Dendy
EPA Basket Type	Comparable date, limited extra material for quick lab processing	No measure of pollution on strata, only community formed in sampling period, long exposure time, difficult to anchor, easily vandalized
EPA Periphyton	Floats on surface, easily anchored, glass slides exposed just below surface	May be damaged by craft; easily vandalized
2. <u>Natural</u>		
Any bottom or sunken material	Indicate effects of pollution, gives indication of long term pollution	May be difficult to Quantitate Possible lack of growth, not knowing previous location or duration of exposure

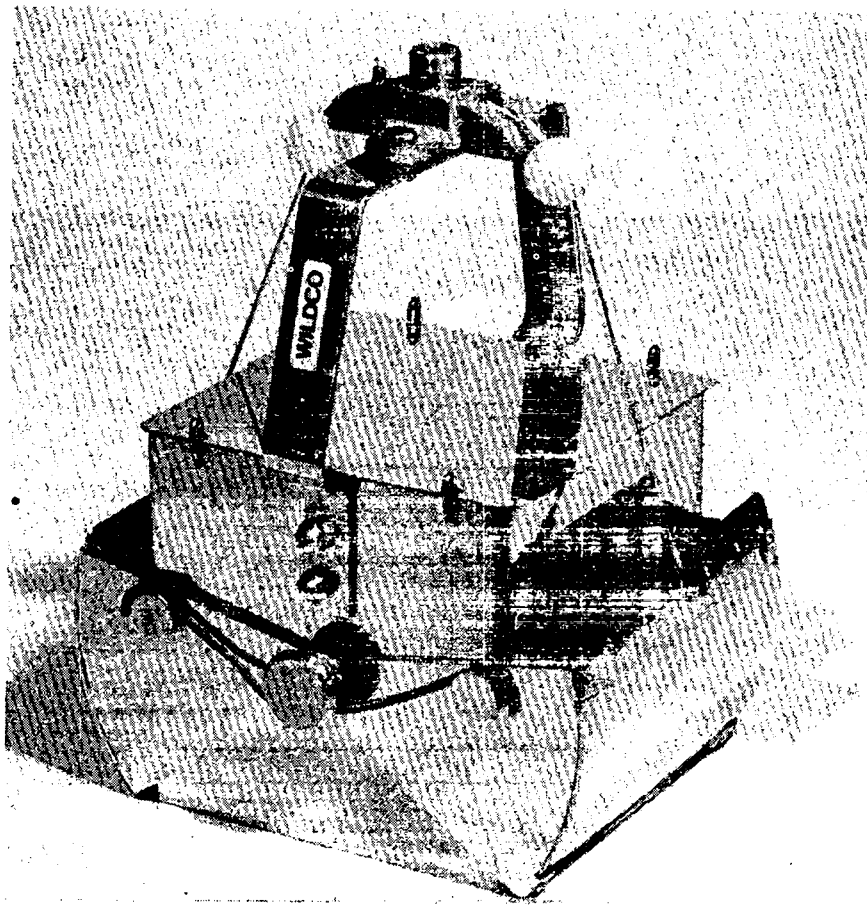


Nansen Water Bottle

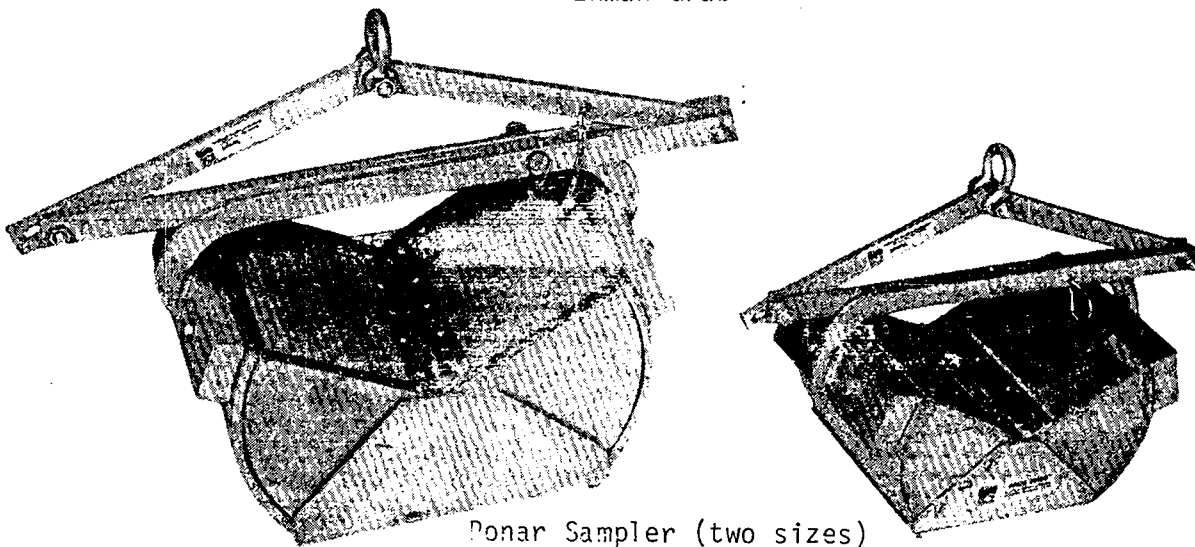


Van Dorn Sampler

8.4 Water Bottles
(Courtesy of Wildlife Supply Co.)

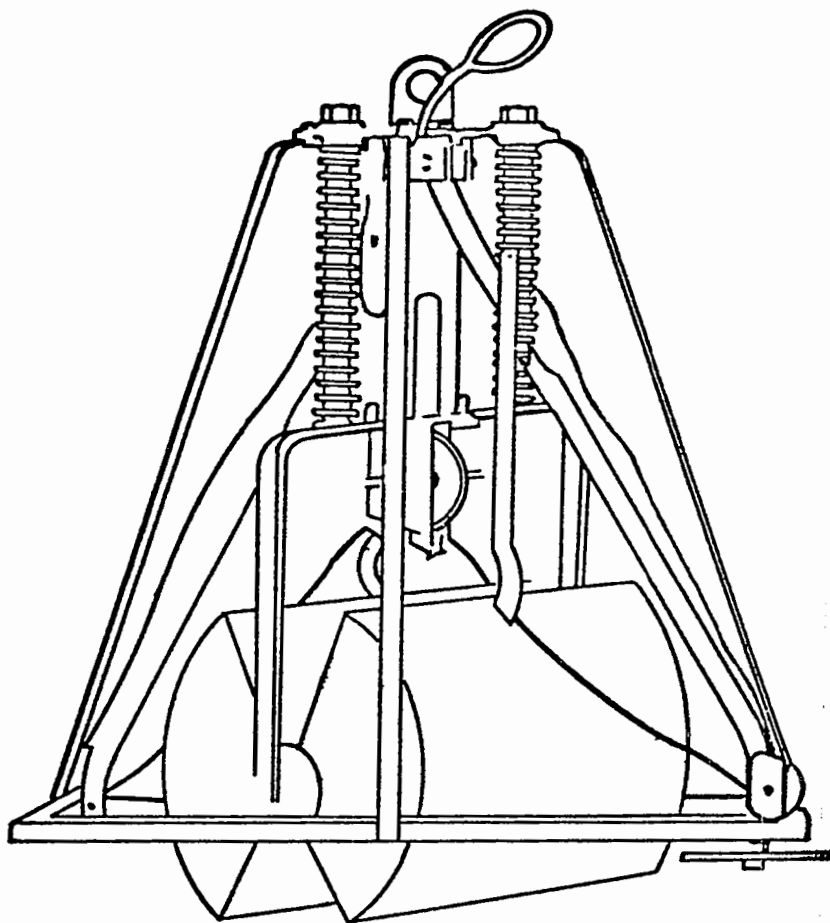


Ekman Grab



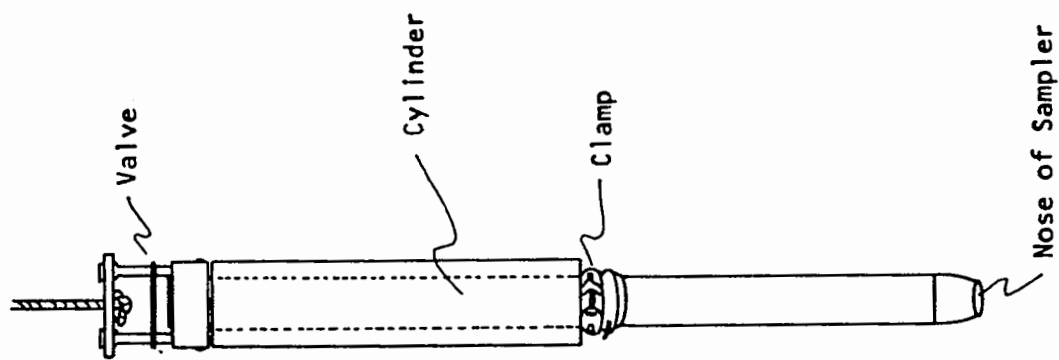
Ponar Sampler (two sizes)

Figure 8.5 Bottom Grab Samplers
(Courtesy of Wildlife Supply Co.)

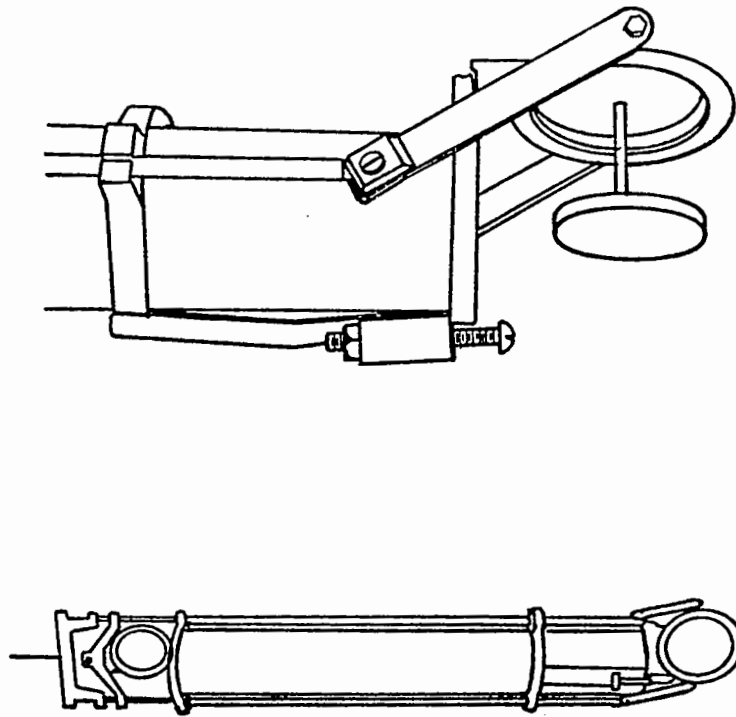


Smith-McIntyre (Aberdeen) Grab

Figure 8.5 (continued) Bottom Grabs

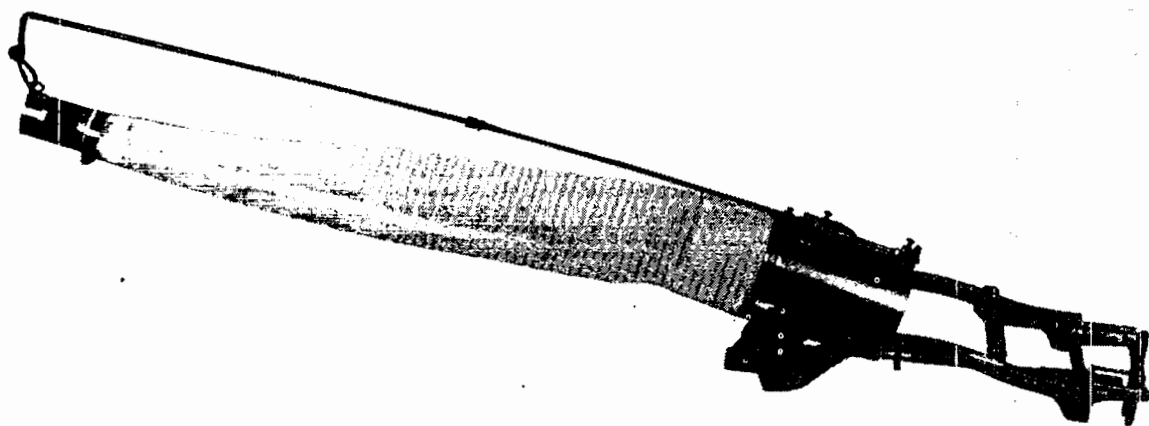


Side View-Vertical Core Sampler

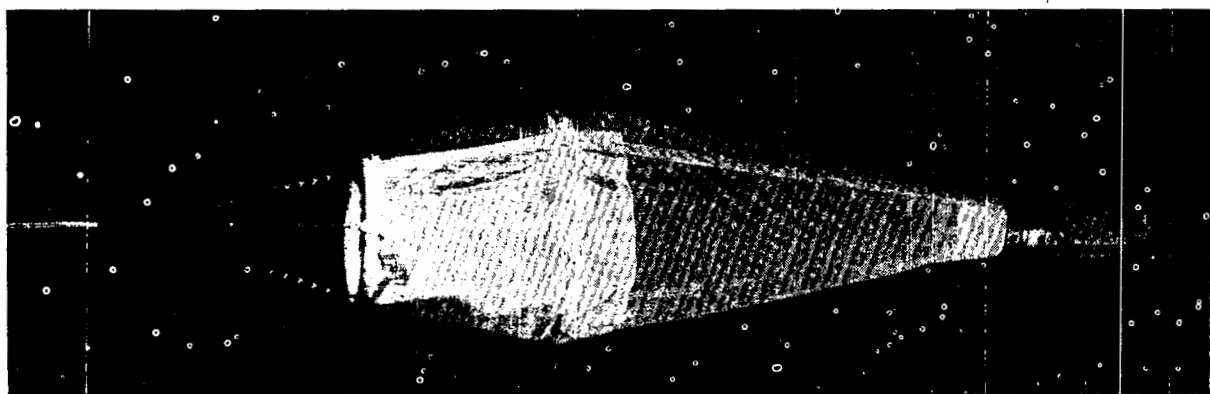


Elgmork's Core Sampler

Figure 8.6. Core samplers

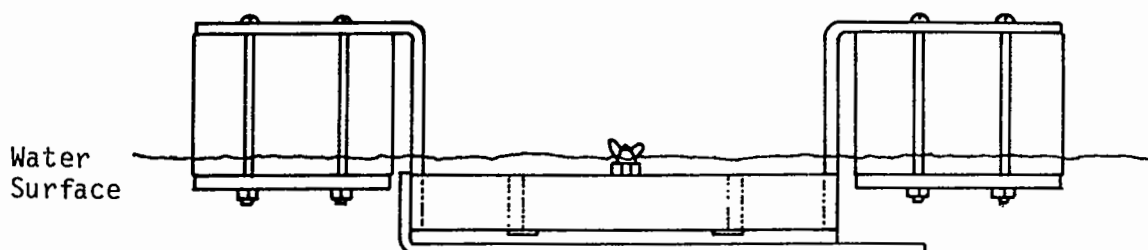


Clark-Bumpus Sampler

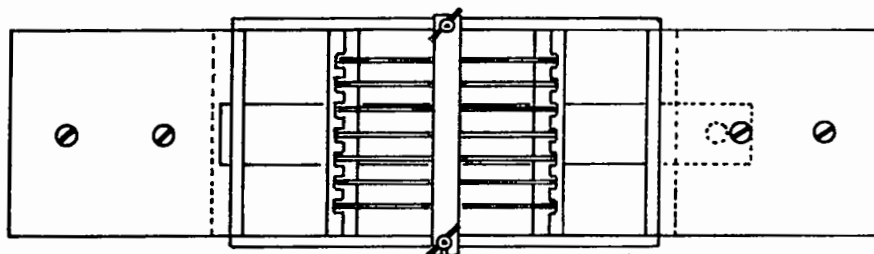


Wisconsin Net

Figure 8.7 Nets and Related Samplers



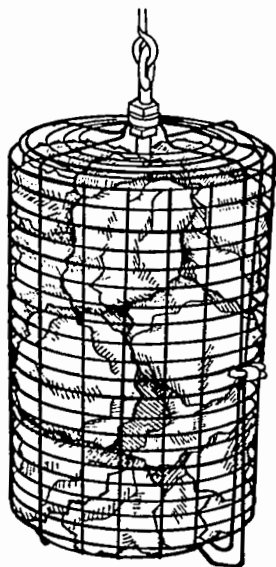
Side View



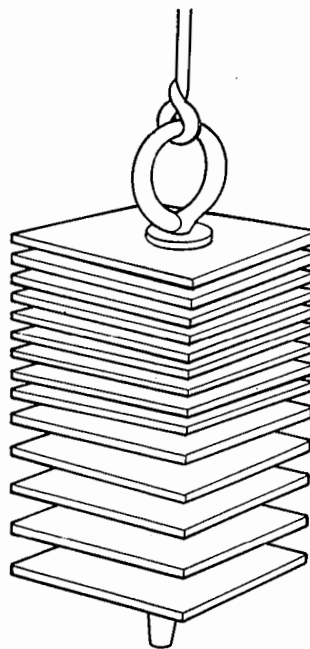
Top View

EPA Periphyton sampler. Plexiglass frame supported by two styrofoam floats. Rack holds eight glass microscope slides.

Figure 8.8 Periphyton samplers



Limestone filled
basket sampler



Modified Hester-Dendy
type multiple-plate
artificial substrate

Figure 8.8 (Continued)

8.10 PRESERVATION HANDLING OF SAMPLES

Refer to Section 17.1 for specific information regarding preservation and handling of samples relative to the chemical parameters to be analyzed, and to the EPA biological methods manual (2) for aquatic organism preservatives.

8.11 FLOW MEASUREMENT

Flow measurement in rivers is accomplished by the combined use of a current meter to measure the stream velocity and a stage recorder to measure the surface elevation of the river. Consult USGS gaging stations for additional or historic information. See Section 3 for more details.

8.12 REFERENCES

1. Weber, C.I., editor. Biological Field and Laboratory Methods for Measuring the Quality of Surface Waters and Effluents. National Environmental Research Center, Office of Research and Development, U.S. EPA, Cincinnati, Ohio, EPA 670/4-73-001, 1973.
2. National Water Monitoring Panel. Model State Water Monitoring Program. U.S. EPA Report No. EPA-440/9/74-002. U.S. EPA Office of Water and Hazardous Materials, June, 1975.
3. Hill, R.F. Planning and Design of a Narragansett Bay Synoptic Water Quality Monitoring System. NEREUS Corp., 1970.
4. Drobny, N.L. Monitoring for Effective Environmental Management. Proc. ASCE National Water Resources Engineering Meeting. Atlanta, Georgia. January 24-28, 1972.

CHAPTER 9

SAMPLING OF GROUND AND DRINKING WATER

9.1 BACKGROUND-GROUND WATER

Ground water accounts for the base flow of all perennial streams, over 90 percent of the world's fresh water resources, and one half the drinking water in the United States, yet has traditionally received only token scientific attention. Although surface and ground waters are inseparable parts of the same hydrologic system with the waters of each flowing alternately between the two components, water resource planners have often considered them as separate entities.

The Safe Drinking Water Act (PL 93-523) of 1974 has done much to rectify this neglect by recognizing ground water quality protection. This Act plus subsequent legislation, the Toxic Substances Control Act (PL 94-469) and the Resource Conservation and Recovery Act (PL 94-580) further recognizes that ground water quality is being increasingly threatened by various human activities, particularly the disposal of waste materials to the land.

In order to assess the impact of such activities on ground water quality and, hence, to provide a rational basis for its protection, the behavior of pollutants in the subsurface and the processes governing this behavior must be evaluated. However, many water resource planners, inexperienced in ground water investigations, are learning that techniques applicable to surface waters do not necessarily apply to ground water.

Methods of collecting a representative ground water sample are much more difficult and expensive in this often remote and relatively inaccessible environment. The subsurface is an extremely complex system subject to extensive physical, chemical and biological changes within small vertical and horizontal distances.

The purpose of this chapter is to provide some of the most prevalent methods of sampling the subsurface and drinking waters. A more detailed and comprehensive discussion of ground water can be found in an unpublished EPA report entitled Manual of Ground Water Quality Sampling Procedures,(1)

9.2 OBJECTIVES OF GROUND WATER SAMPLING

Samples from a monitoring well represent a small part of an aquifer horizontally and in many cases, vertically. Unlike its surface counterpart

where a sample can be arbitrarily taken at any point in the system, moving a ground water sampling point implies the installation of additional monitoring wells. Because of the difficulty and expense, it is essential that sampling objectives be firmly established well in advance of field activities. These objectives will dictate the parameters to be measured, the necessary reliability of the water quality data, and analytical methodology and thence the sampling procedures necessary to meet these objectives.

If the objective is simply to determine the presence or absence of a conservative pollutant in a particular water supply, it is simple and relatively inexpensive to collect a sample at a water tap. However, if the objective is to define the horizontal and vertical distribution of an organic pollutant or pollutants and predict the eventual fate, then soil cores, monitoring wells and special sampling equipment may increase efforts and cost several orders of magnitude.

In the former case, the purpose of the sample collection activity is known and limited in scope. In the latter case, there is a need to be concerned not with point data as an end in itself, but as a component of a network approach wherein information on the ground water system is developed as a basis for extrapolating information to areas where samples were not collected and/or for predicting the effects of natural and man made stresses on the subsurface system.

9.3 GROUND WATER SUBSURFACE CHARACTERISTICS

The unstable nature of many chemical, physical, and microbial constituents in ground water and subsurface limit the sample collection and analyses options. However, certain factors should be considered when collecting representative samples:

1. Ground water moves slowly, therefore a slow rate of change of water quality parameters.
2. Temperatures are relatively constant in the subsurface, therefore the sample temperature may change significantly when brought to the surface. This change can alter chemical reaction rates, reverse cationic and anionic ion exchanges on solids, and change microbial growth rates.
3. A change in pH can occur due to carbon dioxide adsorption and subsequent changes in alkalinity. Oxidation of some compounds may also occur.
4. Dissolved gases such as hydrogen sulfide may be lost at the surface.
5. Integrity of organic samples may be affected by problems associated with either adsorption or contamination from sampling materials and volatility.
6. Both soils and ground waters may be so severely contaminated as to present a health or safety problem to sampling crews.

9.4 LOCATION OF GROUND WATER SAMPLING POINTS

9.4.1 General Considerations

The area of consideration, the time available for monitoring, and potential concentration levels of pollutants all influence the sampling procedures selected. A regional or large area monitoring program may permit the use of existing wells, springs or even the baseflow of streams if these systems are compatible with the parameters of interest. If time is critical, existing sampling locations may be the only alternative. However, if the possible pollution source is relatively small, such as a landfill or lagoon, or if pollutant concentrations may be very low, such as with organics, special monitoring wells will almost surely be necessary. The number and location of additional wells needed depends on the purpose of monitoring, aquifer characteristics, and mobility of pollutants in the aquifer.

If the potential contamination source is above the water table, it may be necessary to sample the unsaturated zone to get a true picture of the threat to ground water. With the exception of chlorides, and to a lesser extent nitrates and sulfates, most pollutants can be sorbed to materials in the unsaturated zone and removed to some extent under favorable conditions. (2) Therefore, it is possible to sample the ground water beneath a waste source for years and observe no contamination. This can give a false sense of security when actually pollutants are still moving very slowly through the unsaturated profile toward the ground water.

9.4.2 Hydrogeologic Data

Geologic factors relate chiefly to geologic formations and their water bearing properties, and hydrologic factors relate to the movement of water in the formations.

Knowledge of the hydrogeologic framework is important from two standpoints: (a) prediction of ground water movement; and (b) geochemical considerations which affect the quality of ground water. The geologic framework includes lithology, texture, structure, and mineralogy, and the distribution of the materials through which ground water flows. The hydraulic properties of the earth materials depend upon their origin and lithology, as well as the subsequent stresses to which the materials have been subjected. Ground water movement depends upon the effective permeability and the hydraulic gradient within an aquifer. Permeability is related to the nature, size and degree of interconnection of pores, fissures, joints, and other openings.

Prior to initiating any field work, all existing geologic and hydrologic data should be collected, compiled and interpreted. Data that may be available include: geologic maps, cross-sections, aerial photographs, and an array of water well data including location, date drilled, depth, name of driller, water level and date, well completion methods, use of well, electric or radioactivity logs, or other geophysical data, formation samples, pumping test(s) and water quality data. After compiling and thoroughly reviewing the collected data, the investigator can properly plan

the type of investigation needed, including the data necessary to fill the gaps and the sampling necessary (parameters, frequency and locations(s)).

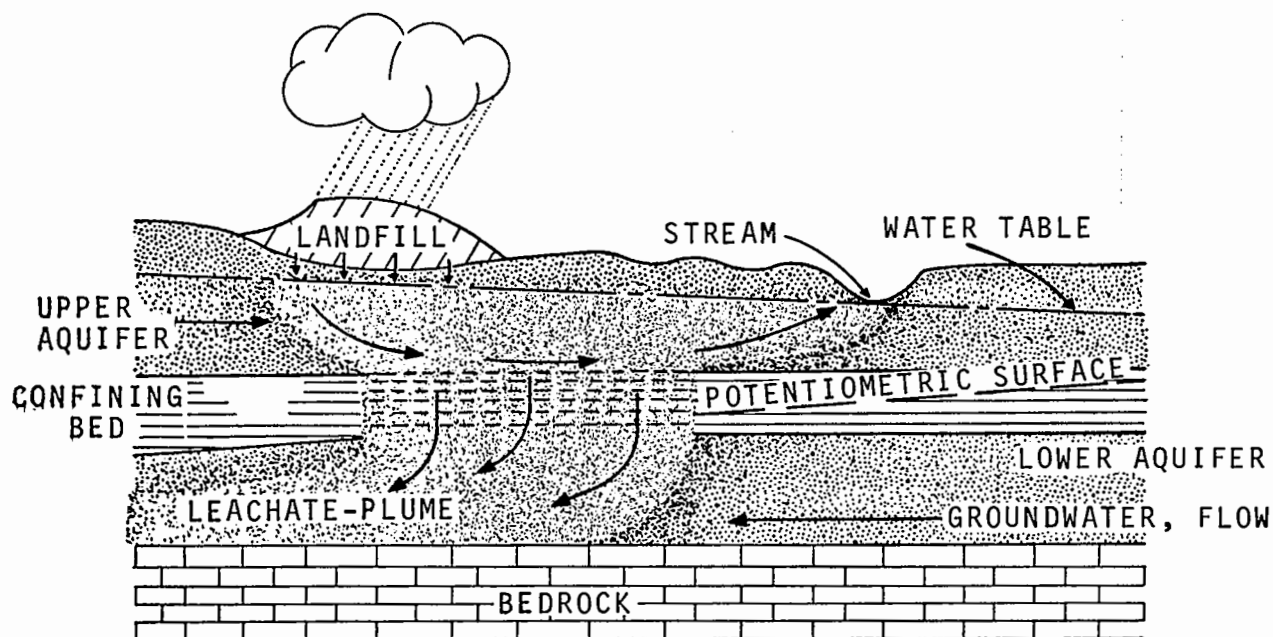
Water level measurements are important basic preliminary data often used in selecting ground-water sampling sites, equipment and procedures. Water level data can be obtained from wells, piezometers, or from surface-water manifestations of the ground water system such as springs, lakes, and streams. The depth of water may determine the type of pumps or samplers used and procedures and cost of constructing monitoring wells. Water level contours drawn from static levels in wells penetrating the same aquifer can be used to make a preliminary determination of gross direction of flow. Note that nearby pumping wells or other artificial discharges or recharges may alter the natural gradient.

9.4.3 Hydrogeologic Considerations

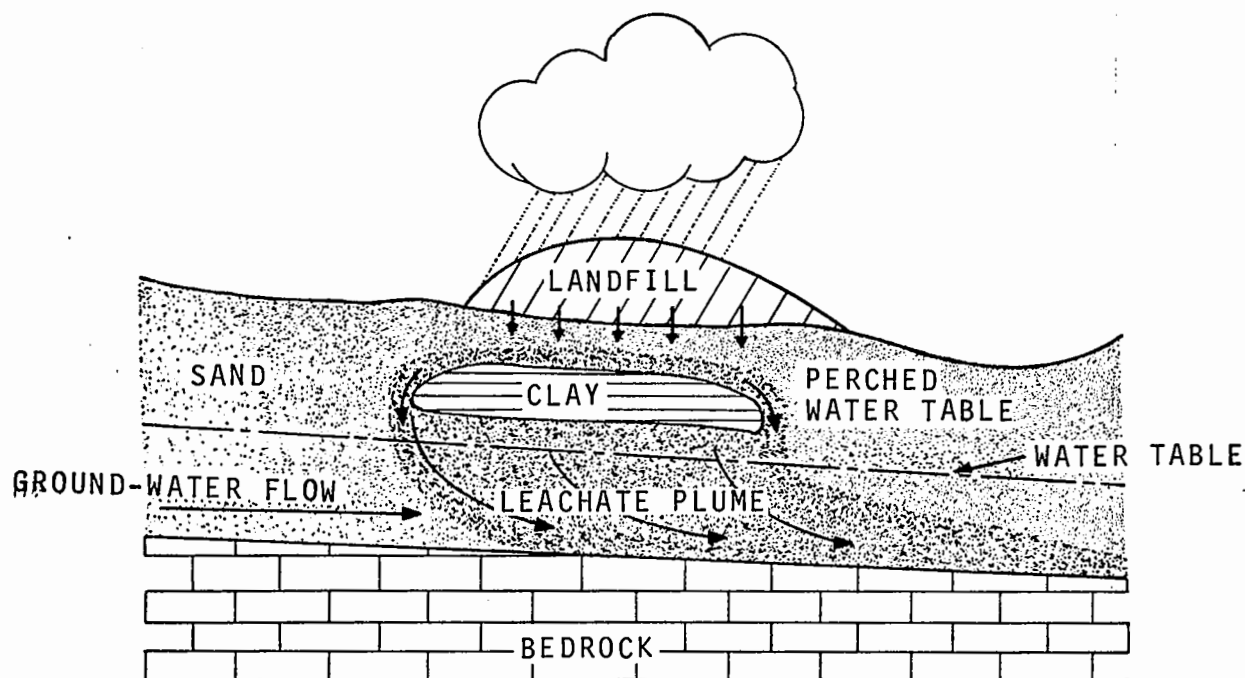
The heterogeneous nature of subsurface environments makes the location of sampling points a complicated and unpredictable science when trying to intercept a pollutant plume. Hydrogeologic conditions are site specific and it is impossible to prescribe standard locations for sampling points that would be applicable to all sites. In an aquifer with intergranular porosity, such as sands, gravels, sandstones and silts, water occurs in interconnected void spaces between individual particles of aquifer material. Some simplified "typical" flow patterns are illustrated in Figure 9.1. It is readily apparent that the horizontal location of a monitoring well in relation to the pollutant source determines whether or not contaminated water is intercepted. Further, vertical location of the well screen and other well construction aspects also affect the quality of a sample collected from the well. Should the well screen be located above or below the zone of contamination, and assuming proper seals are located above and below the screen, samples from this well will very likely indicate no contamination unless it is pumped sufficiently to change the ground water flow pattern. On the other hand, if the well screen is not properly sealed from other subsurface zones or if the entire saturated thickness is screened, samples from the well may represent a composite of water from several different zones and concentrations will not be representative. Furthermore, such well construction may provide a conduit for the movement of contamination from one zone to another.

Ground water flow patterns can be developed from water level contours. However, the actual movement of a plume may be somewhat more complex. For example, in a geologic environment such as alluvium or terrace deposits involving intergranular permeabilities, the shape of the plume may be controlled by abrupt changes in permeabilities such as the channel gravels as shown in Figure 9.2. Such changes in permeability are common in river deposited geologic formations and can greatly affect the shape and rate of movement of pollution plumes.

The hydrogeology is further complicated by the different flow patterns of different pollutants. Ground water contaminated with a dense pollutant such as chloride creates a plume that tends to migrate to the base of the aquifer. Conversely, lighter pollutants such as hydrocarbons tend to "float" near the top of the saturated zone. In addition, different

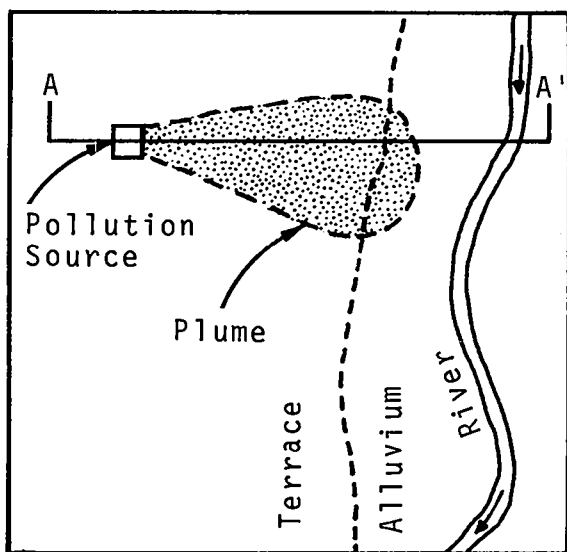


Two-Aquifer System with Opposite Flow Directions. Leachate first moves into and flows with the ground water in the upper aquifer. Some of the leachate eventually moves through the confining bed into the lower aquifer where it flows back beneath the landfill and away in the other direction.

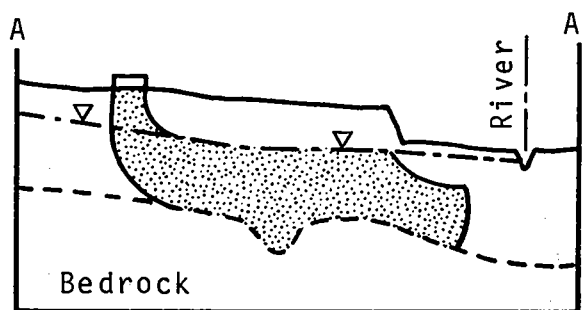


Permeable Sand Layer Underlain by a Clay Layer - The water table is deep. Leachate percolates downward under the landfill, forming a perched water table before finally reaching the actual water table.

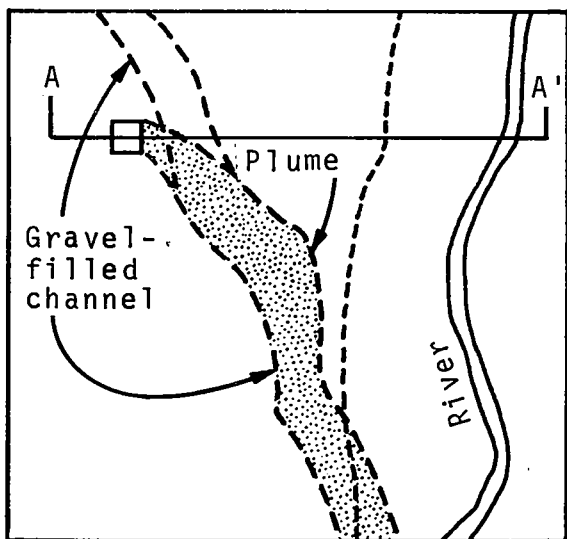
Figure 9.1 Typical Flow Patterns of Pollutant Plumes



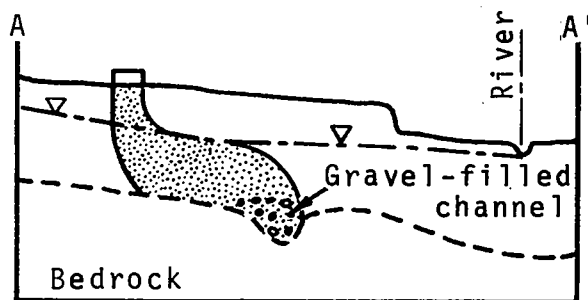
PLAN VIEW



CROSS SECTION



PLAN VIEW



CROSS SECTION

Figure 9.2 Effective of Permeability Change on Shape of Pollution Plume

pollutants move through the subsurface at different rates relative to the rate of water movement because of sorption, desorption, ion-exchange and biodegradation. Therefore, points of maximum concentration of the different pollutants along the ground water flow path will probably vary considerably.

Ground water flow patterns are even less predictable in fractured rock or solution porosity aquifers than in aquifers with intergranular porosity. Flow patterns are generally controlled by fracture patterns such as those illustrated in Figures 9.3. Obviously, the problem in locating monitoring wells in such geology is to intercept fractures or solution channels that are hydraulically connected to the source of contamination. It is possible in many formations of this type to drill a well that is dry and move only a few feet away and drill another that has plenty of water. However, neither well may be hydraulically connected to a source of pollution only a few feet away.

In some fractured rock formations where caving is not a problem it is possible to complete a monitoring well as an open hole without using a well screen. In most such wells it is advisable, however, to install casing (grouted in place) to at least the depth planned to set the pump. Care must be exercised especially in fractured rock formations such as limestone to maintain the depth-specific factor for monitoring wells. Wells with much open hole may intercept several fractured zones resulting in intercommunication between layers and sampling of mixed waters.

In spite of the complexity and in lieu of a detailed hydrogeologic study, there are some basic guidelines that can be used in locating monitoring wells based on the considerations noted previously. A more detailed examination of locating monitoring wells for a landfill is described in Procedures Manual for Ground Water Monitoring at Solid Waste Disposal Facilities .(2)

9.4.4 Background Considerations

A necessary component of any ground water monitoring program is background sampling. Occasionally, it is possible to sample the ground water quality of an area before a source of contamination is introduced. This is desirable and may become more common in the future as ground water quality protection becomes a greater part of normal operations. In most instances, a potential source of contamination is already a reality and the objective is to collect a sample for comparison that is out of the influence of that source. Another consideration is that an analysis of an earlier sample may not have included a parameter that is of current interest or that analytical capabilities may have improved for certain parameters in the meantime.

One recommended monitoring method for detecting contamination at landfills is location of a background well upgradient from the landfill and a minimum of three wells downgradient and at an angle perpendicular to ground water flow, penetrating the entire saturated thickness of the aquifer. Such an arrangement is illustrated in Figure 9.4 and is applicable to most potential point sources of contamination.

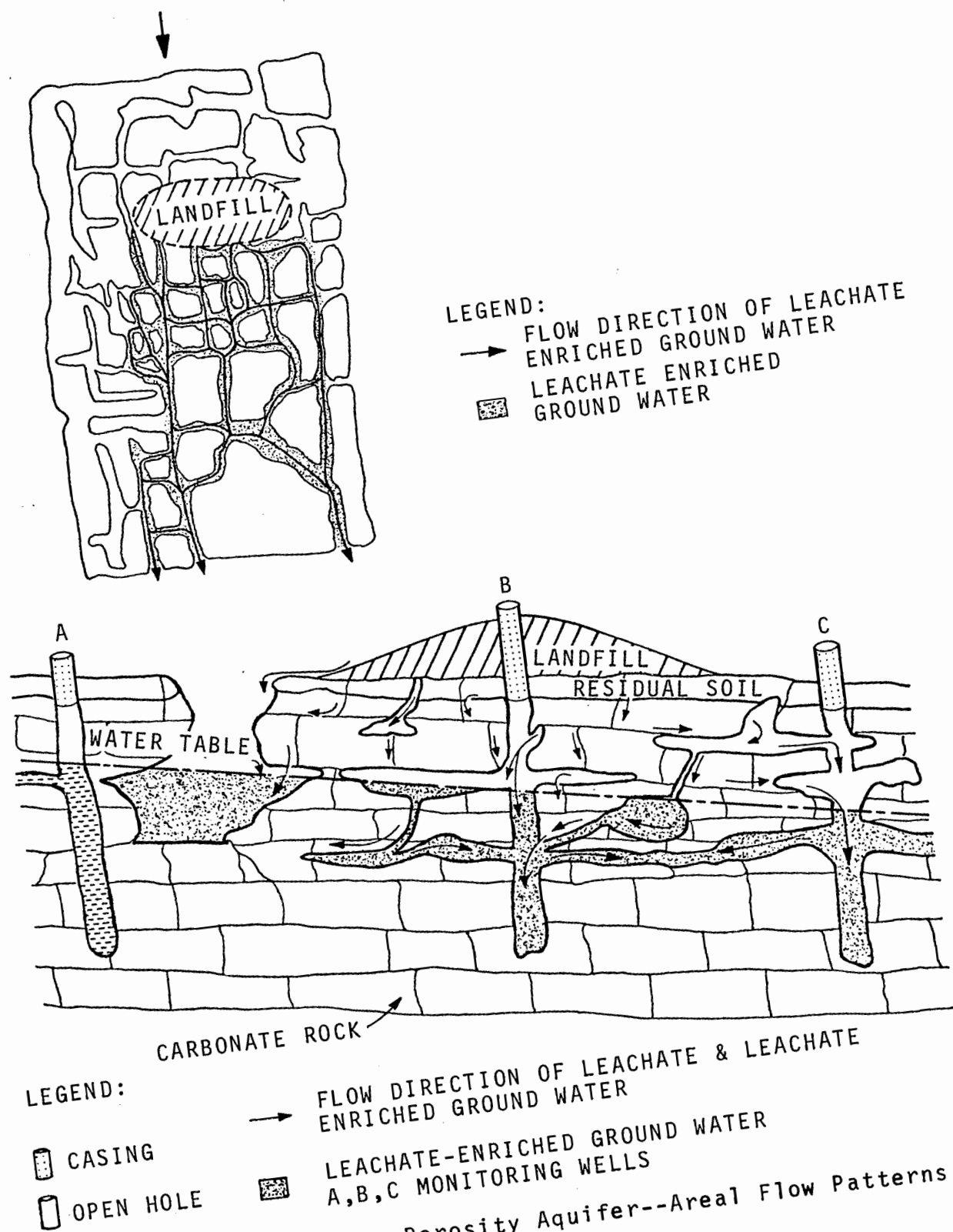


Figure 9.3 Solution Porosity Aquifer--Areal Flow Patterns

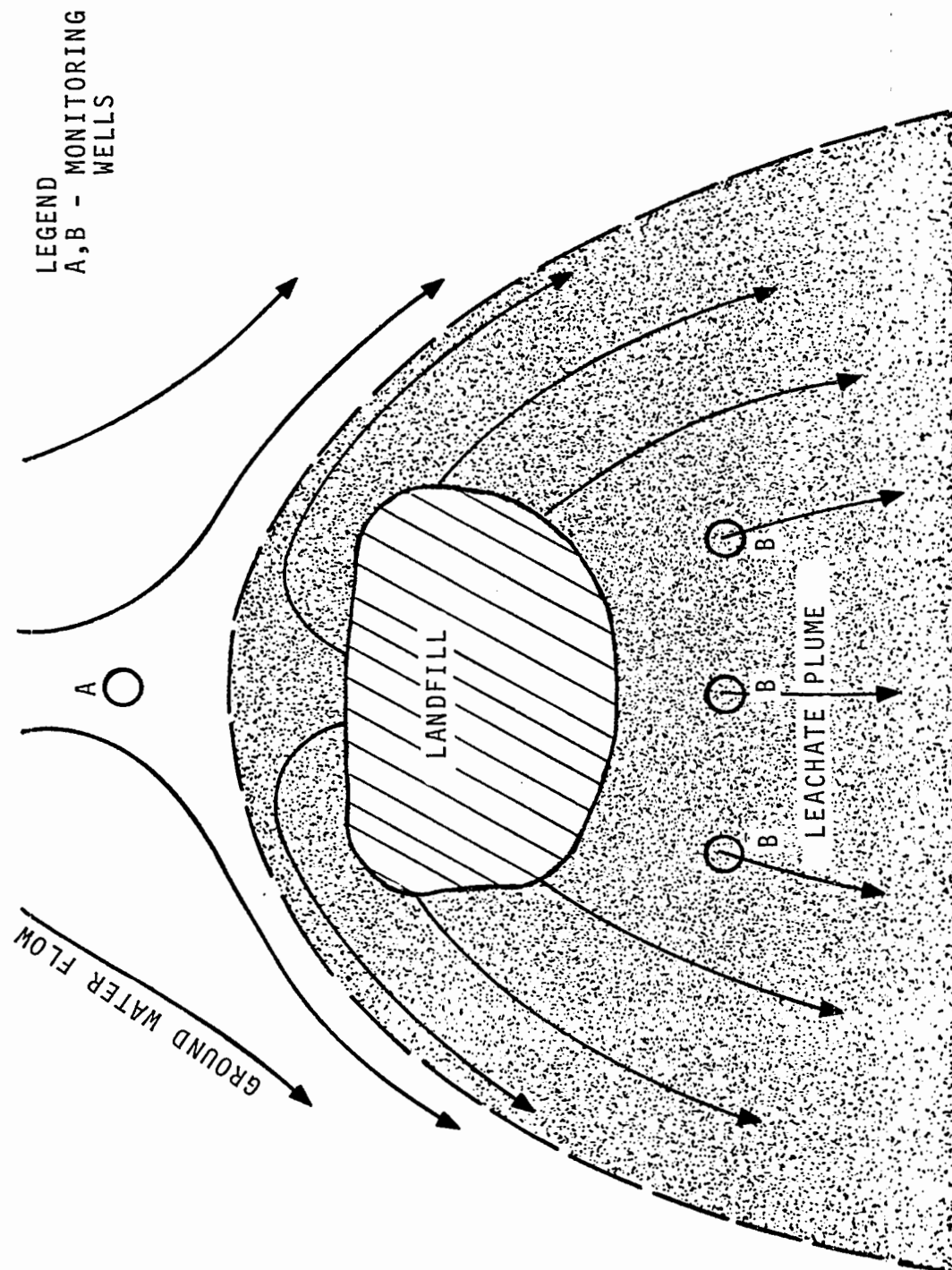


Figure 9.4 Idealized Monitoring Network

If there is adequate reason to suggest that contamination has already occurred and the objective is to define the pollutant plume, this remains a reasonable initial approach. However, it is extremely important to locate subsequent monitoring wells one at a time, sample, and base succeeding well locations on results of previous sampling. Under no circumstances should the entire drilling budget be expended on a series of monitoring wells based entirely on the initial prediction of the direction of a pollutant plume. Even with the best of background information, there is a high probability that a large percentage of these wells will miss the pollutant plume because of the heterogeneous nature of subsurface permeabilities.

9.5 CONSTRUCTION OF GROUND WATER MONITORING WELLS

The success of a ground water monitoring program depends on numerous factors; however, the location, design, and construction of the monitoring well is usually the most costly and non-repeatable factor. Hence it is extremely important that the well construction be accomplished properly at the outset. The primary objective of monitoring wells are: (a) provide access to ground water; (b) determine which pollutants are present in the ground water and their concentrations; and (c) determine the areal and vertical distribution of pollutants. In order to accomplish these objectives in the most competent and cost effective manner, consideration must be given the proper well design and construction method that will best fit the specific objectives and the hydrogeologic conditions.

9.5.1 General Requirements

9.5.1.1 Diameter

The diameter of the casing for monitoring wells should be just sufficient to allow the sampling tool (bailer or pump) to be lowered into the well to the desired depth. The diameter of the hole into which the casing is placed must be at least 2 inches larger to permit placement of a grout seal around the outside of the casing.

Casings and/or holes drilled much larger than the necessary minimum can, in fact, have undesired effects on the data. For example, in formations of very low permeability, the excessive storage in an unnecessarily large boring can cause the water level inside the boring to be erroneously low for days or even weeks. Also, because it is usually necessary to remove water standing in the well before taking a sample of the formation water, excessive storage can complicate the water sampling procedure.

9.5.1.2 Depth

The intake part of a monitoring well should be depth-discrete. That part of the well, the screen or other openings, through which water enters the well or casing should be limited to a specific depth range.

Water supply wells that may exist in an area to be monitored are often used as sampling points. Substantial care must be exercised when this is

done and the results are often questionable. Water supply wells are constructed to produce a given quantity of water, hence, they may be screened throughout a thick aquifer, through several permeable layers of an aquifer, or sometimes through two or more aquifers or discrete water bearing layers. When this situation exists, it is probable that the hydrostatic heads are different between different layers. Under nonpumping conditions, this interconnection permits water from the layer with the higher head to flow through the well and into the formation with the lower head. This can occur between layers of different permeability separated by only a few feet of low permeability material. This condition can, of course, have substantial effect on the concentration of a pollutant obtained by pumping for a short time before sampling.

Therefore, it is important that monitoring wells be constructed to be depth-discrete and to sample only from one specific layer without interconnection to other layers. In order to assure that this depth-discrete requirement is met, provisions for placing cement grout above and, if necessary, below the well screen on the outside of the casing must be made in the design of the wells.

Commonly (especially when sampling for contaminants lighter than water) it is desirable to sample at the water table, or top of the saturated zone in an unconfined aquifer. The screen or intake part of the well should then extend from a few feet above to a few feet below the anticipated position of the water table to allow for future water table fluctuations. Often, under semi confined aquifer conditions, the water will rise in the well above the top of the more permeable layer and above the top of an improperly positioned screen. Care must be exercised in these cases to extend the screen high enough to be above the water level in the formation; otherwise, light organics or other contaminants could be undetected or at least not properly quantified.

On the other hand, a contaminant can migrate along fairly restricted pathways and go undetected by depth-discrete wells which are not completed at the proper depth. This danger is particularly present in a geologic environment of highly stratified formations, and in fractured rock formations.

9.5.1.3 Intake Portion of Monitoring Wells

That part of the well through which water enters the casing must be properly constructed and developed to avoid subsequent sampling problems. Commercially made well screens used in water supply wells are recommended for most monitoring wells even though well efficiency is not a primary concern. Other choices are sawed or torch cut slots in the well casing to let the water flow in. The design criteria for the intake part of the well are:

- (1) The screen or intake part should have sufficient open area to permit the easy inflow of water from the formation
- (2) The slot openings should be just small enough to keep most of the natural formation out, but as large as possible to allow

- easy flow of water.
- (3) The well should be developed.

9.5.1.4 Well Casing

Sampling equipment, including well casings, should be constructed of materials that have the least potential for affecting the quality parameters of the sample. The usual dilemma for the field investigator is the relation between cost and accuracy. Obviously, PVC is far less costly than Teflon, a major consideration when contemplating well construction for a major ground water monitoring effort. On the other hand, bleeding of organic constituents from PVC cements, as well as adsorption, poses a significant potential for affecting the quality of samples where the contaminants under consideration may be in the parts per billion range.

In many situations, it may be realistic to compromise some accuracy with cost, particularly in regard to casing materials used in well construction. For example, if the major contaminants are already defined and they do not include substances which might bleed from PVC or cemented joints, it might be reasonable to use wells cased with the less expensive and readily obtainable PVC. Or, wells constructed of less than optimum materials might be used with a reasonable level of confidence for sampling if at least one identically constructed well was available in a nearby, uncontaminated part of the aquifer to provide ground water samples for use as "blanks." Obviously, such a "blank" will not address the problems of adsorption on the casing material nor leaching of casing material induced by contaminants in the ground water. Careful consideration is required in each individual case, and the analytical laboratory should be fully aware of construction materials used.

Care must be given to preparation of the casing and well screens prior to installation. As a minimum, both should be washed with a detergent and rinsed thoroughly with clean water. Care should also be taken that these and other sampling materials are protected from contamination by using some type of ground cover such as plastic sheeting for temporary storage in the work area.

9.5.1.5 Drilling Methods

Selection of the drilling method best suited for a particular job is based on the following factors in order of importance:

1. Hydrogeologic Environment
 - (a) Type(s) of formation(s)
 - (b) Depth of drilling
 - (c) Depth of desired screen setting below water table
2. Types of pollutants expected
3. Location of drilling site; dry land or inside a lagoon
4. Design of monitoring well desired
5. Availability of drilling equipment

The principles of operation, advantages and disadvantages of the more common types of drilling techniques suitable for constructing ground water monitoring wells are discussed in detail in the manual of Ground Water Quality Sampling Procedures.(1)

9.5.1.6 Use of Bore Hole Geophysics

The use of geophysics can greatly enhance the amount of information gained from a borehole as shown in Figure 9.5. Each geophysical logging method is designed to operate in specific borehole conditions, involves lowering a sensing device into the borehole and can be interpreted to determine lithology, geometry, resistivity, bulk density, porosity, permeability, moisture content and to define the source, movement, chemical and physical characteristics of ground water.(3)

1. Spontaneous Potential Log: These logs are records of the natural potentials developed between the borehole fluid and the surrounding rock/soil materials. The SP log is mainly used for geologic correlation, determining bed thickness and separating non porous from porous rocks in shale sandstone and shale carbonate sequences. It can be run only in open, uncased and fluid filled boreholes.
2. Normal Resistivity Logs: Normal logs measure the apparent resistivity of a volume of rock/soil surrounding. The short normals give good vertical detail and records the apparent resistivity of the mud invaded zone. The log normals record the apparent resistivity beyond the invaded zone. The radius of investigation is generally equal to the distance between the borehole current and measuring electrodes. These logs can be run only in open, uncased and fluid filled boreholes.
3. Natural Gamma Logs: Natural gamma logs or gamma ray logs are records of the amount of natural gamma radiation emitted by rocks/soils. The main use of this logging method is for the identification of lithology and stratigraphic correlation. These logs can be run in open or cased, fluid or air filled boreholes. The radius of investigation extends to about 6 to 12 inches of the borehole wall.
4. Gamma Gamma logs: These logs record the intensity of gamma radiation from a source in the probe after it is backscattered and attenuated within the borehole and surrounding rocks/soil. The main uses of gamma gamma logs are for identification of lithology and measurement of bulk density and porosity of rocks/soils. They are also used for locating cavities and cement outside the casing. The radius of investigation is about 6 inches from the borehole wall. These logs can be run in open or cased, fluid or air filled boreholes.
5. Caliper Log: A caliper log is the record of the average borehole diameter. Its major use is to evaluate the environment in which other logs are made in order to correct for hole diameter effects. They also provide information on lithology and borehole conditions. Caliper logs can be run in fluid or air filled, cased or open boreholes.

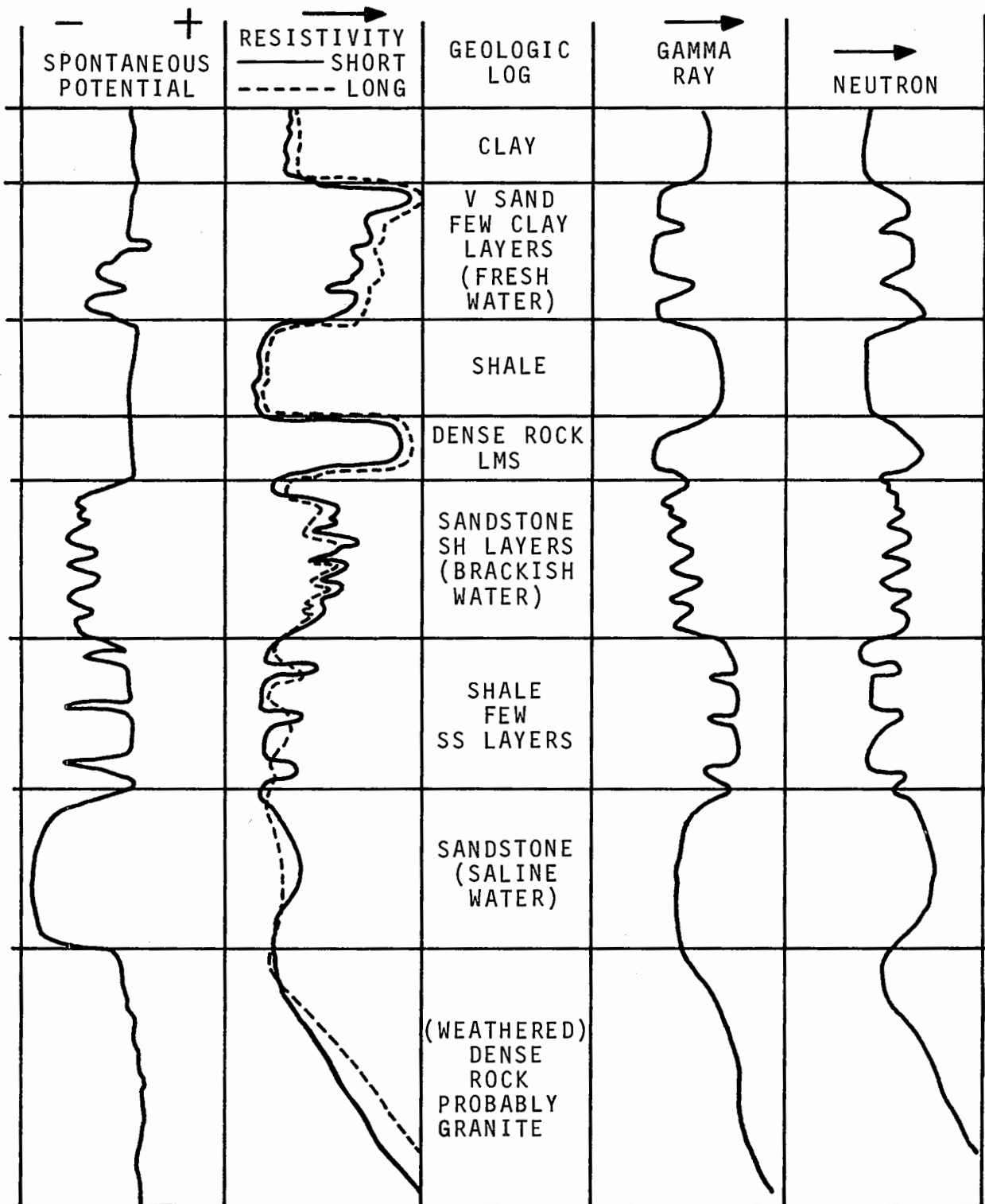


Figure 9.5 Comparison of Electric and Radioactive Bore Hole Logs

6. Temperature Log: These logs provide a continuous record of the fluid temperature immediately surrounding the probe. The data can be interpreted to provide information on the source and movement of ground water and the thermal conductivity of rocks/soils. Temperature logs are best applied in fluid filled, open boreholes although they can also be run in air filled and cased boreholes. The zone of investigation is limited to that fluid immediately surrounding the probe which may or may not be representative of the temperature in the surrounding rock/soils.
7. Fluid Conductivity Logs: These logs provide a measurement of the conductivity of the borehole fluid between the electrodes in the probe. When properly corrected, they provide information on the chemical quality of the borehole fluid. They are best applied in open, fluid filled boreholes.

9.5.1.7 Well Development

Well development is the process of cleaning the face of the borehole and the formation around the outside of the well screen to permit ground water to flow easily into the monitoring well. During any drilling process, the side of the borehole becomes smeared with clays or other fines. This plugging action substantially reduces the permeability and retards the movement of water into the well screen. If these fines are not removed, especially in formations having low permeability, it then becomes difficult and time consuming to remove sufficient water from the well before obtaining a fresh ground water sample because the water cannot flow easily into the well.

The development process is best accomplished for monitoring wells by causing the natural formation water inside the well screen to move vigorously in and out through the screen in order to agitate the clay and silt, and move these fines into the screen. The use of water other than the natural formation water is not recommended. Methods suitable for the development of monitoring wells are discussed in detail in the Manual of Ground Water Quality Sampling Procedures.(1)

9.5.1.8 Multiple Completion Sampling Wells

Occasionally, it is desired to sample numerous permeable layers at considerable depth, perhaps at a few hundred feet. If, for example, it is desired to define the bottom of the pollution plume and then to periodically sample the lower most contaminated layer, a cemented and gun-perforated well can be constructed. Or, if permanent monitoring in several deep layers is required such as for underground injection wells, then the permanent type multiple completion well should be considered.

Figure 9.6 illustrates the construction of a gun-perforated well. This type of well is commonly drilled and logged to define the depth of all the permeable layers. The casing is installed with centralizers and cement grout is placed in the annulus from the bottom up to surround the casing. The grout prevents intercommunication between permeable layers along the outside of the casing. Other types of multicompletion wells are covered in

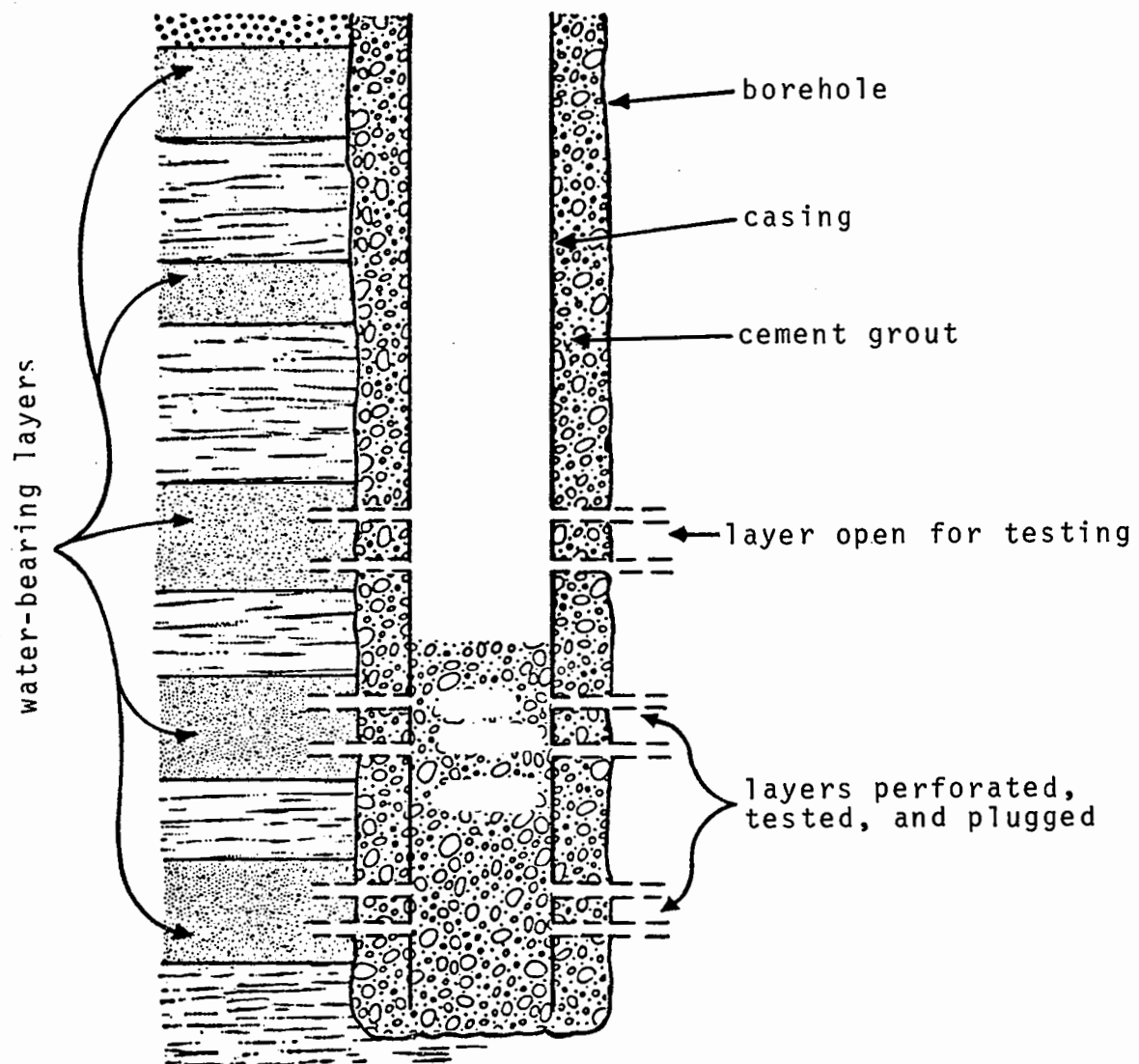


Figure 9.6 Multiple Completion Well, for One-Time Sampling

detail in the Manual of Ground Water Quality Sampling Procedures.(1)

9.6 COLLECTION OF GROUND WATER SAMPLES

The importance of proper sampling of wells cannot be overemphasized. Even though the well being sampled may be correctly located and constructed, special precautions must be taken to ensure that the sample taken from that well is representative of the ground water at that location and that the sample is neither altered nor contaminated by the sampling and handling procedure.

9.6.1 Representative Samples

To obtain a representative sample of the ground water it must be understood that the composition of the water within the well casing and in close proximity to the well is probably not representative of the overall ground water quality at that sampling site. This is due to the possible presence of drilling contaminants near the well and because important environmental conditions such as the oxidation reduction potential may differ drastically near the well from the conditions in the surrounding water bearing materials. For these reasons it is highly desirable that a well be pumped or bailed until the well is thoroughly flushed of standing water and contains fresh water from the aquifer. The recommended length of time required to pump or bail a well before sampling is dependent on many factors including the characteristics of the well, the hydrogeological nature of the aquifer, the type of sampling equipment being used, and the parameters being sampled. The time required may range from the time needed to pump or bail one bore volume to the time needed to pump several bore volumes. A common procedure is to pump or bail the well until a minimum of four to ten bore volumes have been removed.

Other factors which will influence the time required to flush out a well before sampling include the pumping rate and the placement of the pumping equipment within the column of water in the well bore. Care should be taken to ensure that all of the water within the well bore is exchanged with fresh water. For example, recent studies have shown that if a pump is lowered immediately to the bottom of a well before pumping, it may take some time for the column of water above it to be exchanged if the transmissivity of the aquifer is high and the well screen is at the bottom of the casing. In such cases the pump will be pumping primarily water from the aquifer. Gibb notes that removing all water from the well bore is only possible if the well is pumped dry and suggests two alternative approaches: (a) monitor the water level in the well while pumping. When the water level has "stabilized" most if not all of the water being pumped is coming from the aquifer; (b) monitor the temperature and pH of the water while pumping. When these two parameters "stabilize," it is probable that little or no water from casing storage is being pumped.

9.6.2 Sample Collection

This section is primarily concerned with the collection of water

samples from the saturated zone of the subsurface. The type of system used is a function of the type and size of well construction, pumping level, type of pollutant, analytical procedures and presence or absence of permanent pumping fixtures. Ideally, sample withdrawal mechanisms should be completely inert; economical to manufacture; easily cleaned, sterilized and reused; able to operate at remote sites in the absence of external power sources; and capable of delivering continuous but variable flow rates for well flushing and sample collection.

Most water supply wells contain semi permanently mounted pumps which limit the options available for ground water sampling. Existing in place pumps may be line shaft turbines, commonly used for high capacity wells; submersible pumps very commonly used in domestic wells for high head, low capacity applications, and more recently for municipal and industrial uses; and jet pumps commonly used for shallow, low capacity domestic water supplies. The advantage of in place pumps are that water samples are readily available and non representative stagnant water in the well bore is generally not a problem. The disadvantages are that excessive pumping can dilute or increase the contaminant concentrations from what is representative of the sampling point, that water supply wells may produce water from more than one aquifer, and contamination and/or adsorption may be a problem when sampling for organics.

The advantage to collecting water samples from monitoring wells without in place pumps is in the flexibility of selecting equipment and procedures. The principal disadvantage is the possibility of a non representative sample either through collecting stagnant water that is in the well bore or introducing contamination from the surface by the sampling equipment or procedures.

9.6.2.1 Bailers

One of the oldest and simplest methods of sampling water wells is the use of bailers. A bailer may be in the form of a weighted bottle or capped length of pipe on a rope or some modification thereof which is lowered and raised generally by hand. Two examples are represented in Figures 9.7 and 9.8. The modified Kemmerer Sampler is often used for sampling surface waters as well as ground waters. The Teflon bailer was developed specifically for collecting ground water samples for volatile organic analysis.

Advantages of Bailers:

1. It can be constructed from a wide variety of materials compatible with the parameter of interest.
2. Economical and convenient enough that a separate bailer may be dedicated to each well to minimize cross contamination.
3. No external power source required.
4. Low surface to volume ratio reduces outgassing of volatile organics.

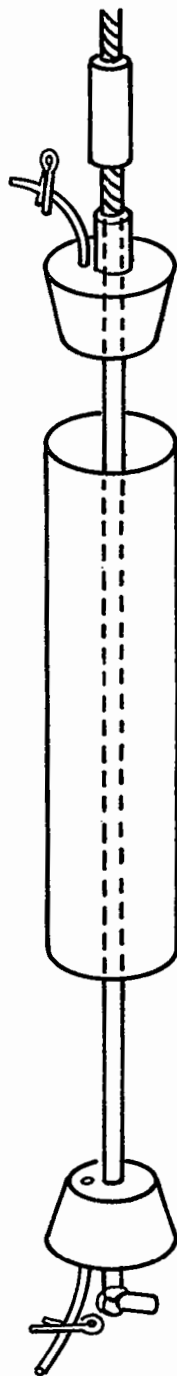


Figure 9.7 Modified Kemmerer Sampler

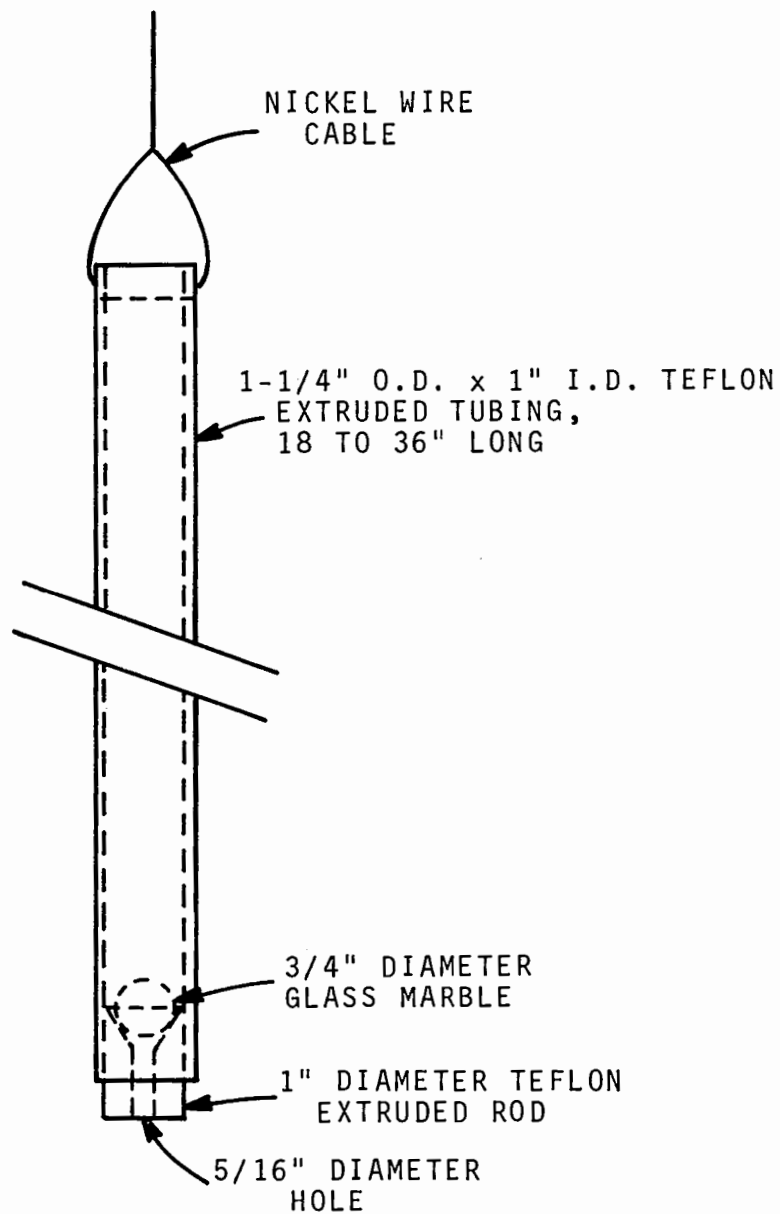


Figure 9.8 Teflon Bailer

Disadvantages of Bailers:

1. Sometimes impractical to evacuate stagnant water in a well bore with a bailer.
2. Transfer of water sample from bailer to sample bottle can result in aeration.
3. Cross-contamination can be a problem if equipment is not adequately cleaned after each use.

9.6.2.2 Suction Lift Pumps

There are a variety of pumps available that can be used when the water table is within suction lift, i.e., less than about 20 feet. Centrifugal pumps are the most commonly available, are highly portable and have pumping rates from 5 to 40 gpm. Most of these require a foot valve on the end of the suction pipe to aid in maintaining a prime.

Peristaltic pumps are generally low volume suction pumps suitable for sampling shallow, small diameter wells. Pumping rates are generally low but can be readily controlled within desirable limits. One significant limitation is the low pumping rates used initially to flush out the well bore. Another limitation is that electrical power is required. Hand operated diaphragm pumps are available that can be operated over a wide range of pumping rates which facilitates rapid evacuation of a well bore initially and lower controlled pumping rates for subsequent sampling. One major advantage is portability.

Advantages:

1. Generally, suction lift pumps are readily available, relatively portable, and inexpensive.

Disadvantages:

1. Sampling is limited to ground water situations where water levels are less than about 20 feet.
2. May result in degassing and loss of volatile compounds.

9.6.2.3 Portable Submersible Pumps

Ground water investigations routinely require the collection of samples from depths which often exceed the limitations of conventional sampling equipment. One such system consists of a submersible pump which can be lowered or raised in an observation well, using 300 feet of hose that supports the weight of the pump, conveys the water from the well, and houses the electrical cable and an electrical winch and spool assembly. A portable generator provides electricity for both the pump and the winch and the entire assembly can be mounted in a pickup or van.

Advantages:

1. Portable. Can be used to sample several monitoring wells in a

- brief period of time.
2. Dependent upon size of pump and pumping depths, relatively large pumping rates are possible.

Disadvantages:

1. Submersible pumps currently available require a minimum well casing inside diameter of three inches.
2. Requires the services of a relatively large service type vehicle, either a van or truck.
3. With conventional construction materials, it is not suitable for sampling for organics.

9.6.2.4 Air Lift Samplers

There are a number of adaptations to the basic method of applying air pressure to a water well to force a water sample out the discharge tube. A high pressure hand pump and any reasonably flexible tubing can be used as a highly portable sampling unit. A small air compressor and somewhat more elaborate piping arrangements may be required at greater depths as shown in Figure 9.9. The primary limitation to this sampler is the potential alteration of water quality parameters, the amount of air pressure that can be safely applied to the tubing and finding a suitable source of compressed air.

Advantages:

1. Can be used as portable or permanently installed sampling system.
2. Can be used to both pre pump and sample.

Disadvantages:

1. Not suitable for pH sensitive parameters such as metals.
2. If air or oxygen is used, oxidation is a problem.
3. Gas stripping of volatile compounds may occur.

9.6.2.5 Nitrogen Powered, Continuous Delivery, Glass and Teflon

With the interest in sampling ground water for trace organic pollutants has come the need for a noncontaminating, nonadsorbing pump for collecting samples below the suction lift. Based on an initial design by Stanford University, Rice University has developed a ground water sampling system consisting of a two stage all glass pump connected by Teflon tubing and powered by nitrogen gas. The system contains four basic units as shown in Figure 9.10: (a) a two stage glass pump; (b) solenoid valve and electronic timer; (c) nitrogen tank and regulator; and (d) columns for organic removal from the ground water.

Advantages:

1. Portable, AC power not required.

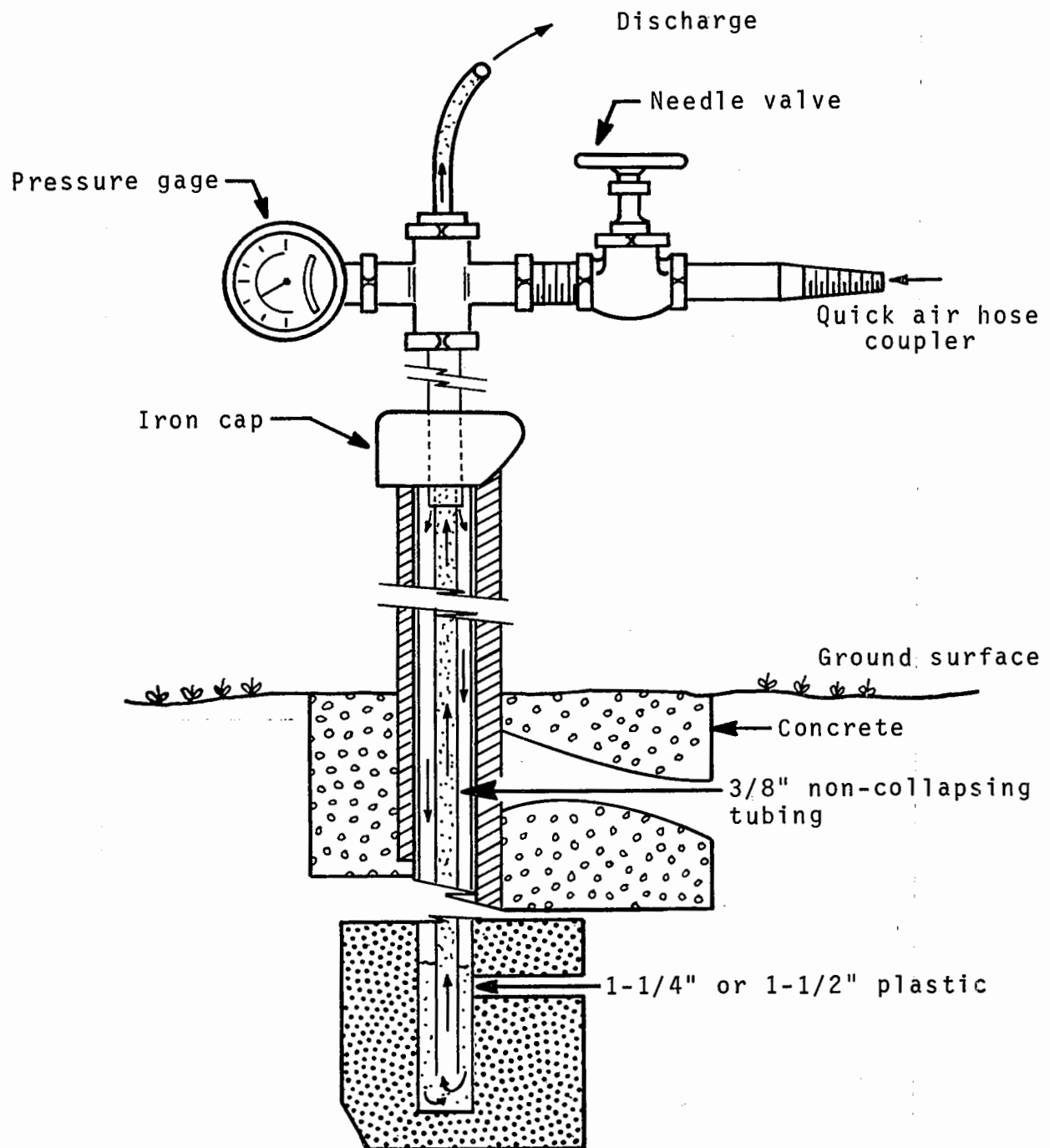


Figure 9.9 Air-Lift Sampler

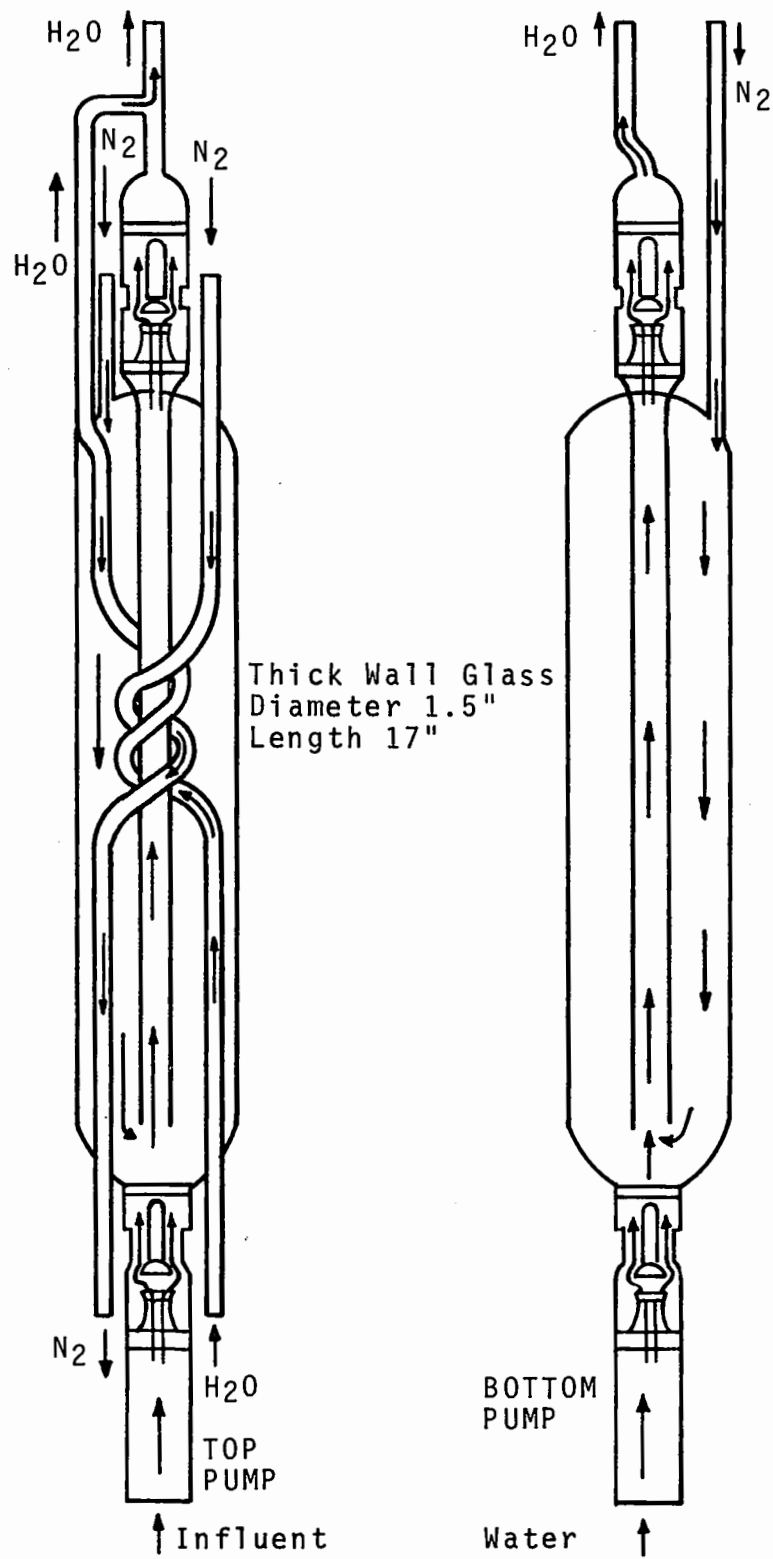


Figure 9.10 Nitrogen Powered, Glass-Teflon Pump

2. Constructed of noncontaminating, nonadsorbing materials.
3. Variable flow rates up to 45 gallons/hour are obtainable.
4. Can be used in well casings with minimum diameters of about two inches.

Disadvantages:

1. Requires high purity nitrogen gas.
2. Glass construction is somewhat more fragile than other materials.
3. Stripping of CO₂ from water may be a problem for pH sensitive parameters.
4. Gas stripping of volatile compounds may occur.

9.6.2.6 Gas Operated Squeeze Pump

These systems consist principally of a collapsible membrane inside a long rigid housing, compressed gas supply and appropriate control valves. When the pump is submerged, water enters the collapsible membrane through the bottom check valve. After the membrane has filled, gas pressure is applied to the annular space between the rigid housing and membrane, forcing the water upward through a sampling tube. When the pressure is released, the top check valve prevents the sample from flowing back down the discharge line, and water from the well again enters the pump through the bottom check valve. A diagram of the basic unit is shown in Figure 9.11.

Advantages:

1. Wide range in pumping rates are possible.
2. Wide variety of materials can be used to meet the needs of the parameters of interest.
3. Driving gas does not contact the water sample, eliminate possible contamination or gas stripping.
4. Can be constructed in diameters as small as one inch and permits use of small economical monitoring wells.
5. Highly portable.

Disadvantages:

1. Large gas volumes and long cycles are necessary for deep operation.
2. Pumping rates cannot match rates of submersible, suction or jet pumps.
3. Commercial units relatively expensive; approximately \$1000 for units currently available.

9.6.2.7 Gas Driven Piston Pump

A modification of pumps developed by Bianchi (4) and Smith (5) has been reported by Signor (6) for collecting samples from wells of two inch or larger diameter. The pump is a double acting piston type operated by compressed gas. The driving gas enters and exhausts from the gas chambers

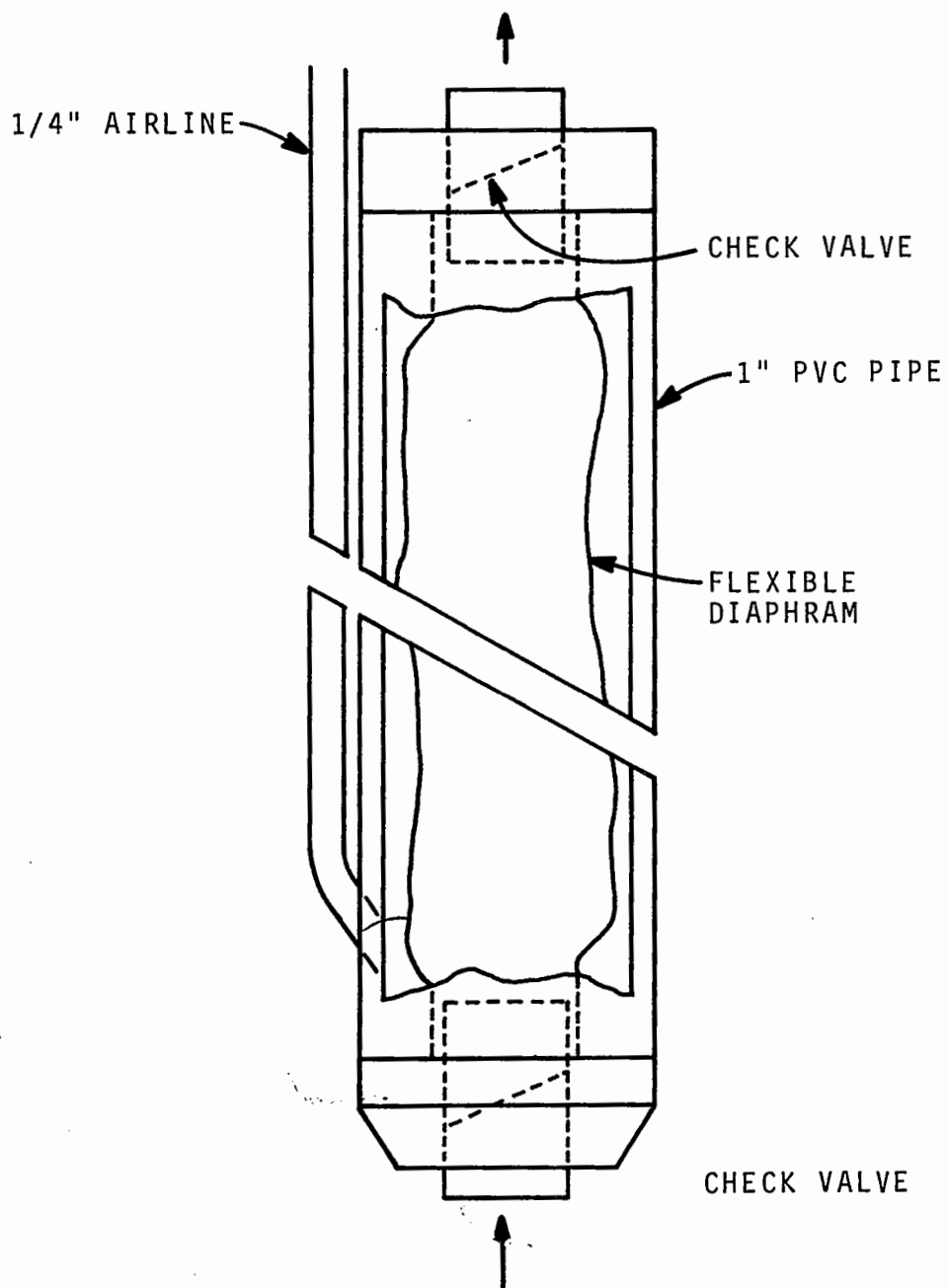


Figure 9.11 Gas-Operated Squeeze Pump

between the two pistons and the intermediate connector that joins them. Built in check valves at each end of the pump allow water to enter the cylinders on the suction stroke and to be expelled to the surface on the pressure stroke. Present designs are constructed basically of stainless steel, brass and PVC. Pumping rates vary with the pumping head but pumping rates of 2.5 to 8 gallons/hour have been noted at 100 feet of pumping head.

Advantages:

1. Isolates the sample from the operating gas.
2. Requires no electrical power source.
3. Operates continuously and reliably over extended periods of time.
4. Uses compressed gas economically.
5. Can be operated at pumping heads in excess of 500 meters.

Disadvantages:

1. Relatively expensive; in excess of \$3000 for the continuously operating unit.
2. Particulate material may damage or inactivate pump unless the suction line is filtered.
3. Low pumping rates.

9.6.2.8 Special Sampling Considerations For Organic Samples (7)(8)

Sampling for organic parameters is a new and in no way, a routine procedure at this time. The equipment and methods in current use are largely in the research state. The concepts are fundamental, however, and any particular item can be modified to suit actual field needs. Furthermore, these rather expensive and sophisticated procedures may not be necessary for sampling or monitoring all areas. New techniques and materials are continuously being examined, which in turn should lead to the development of more sophisticated yet more economical sampling methods. The points that must be kept in mind include the potential for sample contamination and the extremely fine detail, subject to expert rebuttal, that may be necessary in a legal action.

9.6.2.9 Grab Samples

Grab samples of ground water for non volatile organic analysis may be collected by utilizing the system shown in Figure 9.12 where the sampled water contacts only sterile glass and Teflon, and the water table is within suction lift. The sampled water is then carefully transferred to appropriate glass sample containers for shipment to the laboratory.

For sampling at depths beyond suction lift, a noncontaminating submersible pump should be used to pump the ground water to the surface, through scrupulously cleaned Teflon tubing, directly into appropriate sample containers.

The most commonly employed sample containers are 40 mL glass vials for

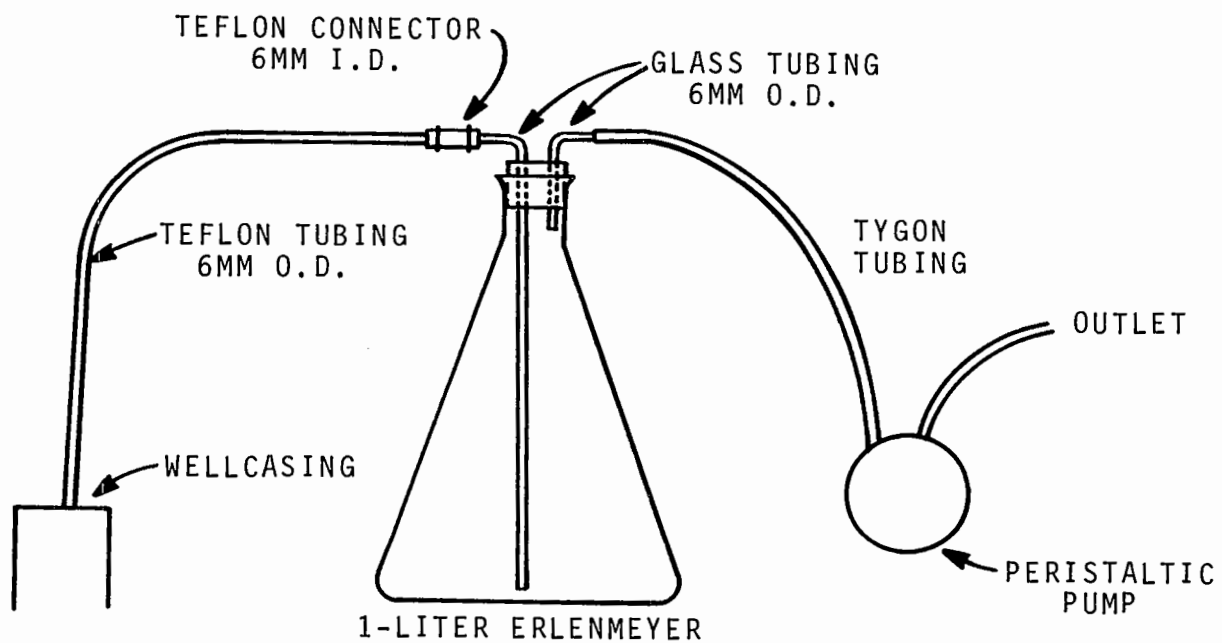


Figure 9.12 System for Grab Sampling

analyses requiring small sample volumes, such as extractable organics. Both types of containers are equipped with Teflon lined screw caps. Like all glassware used in the sampling and analytical procedures, sample containers are thoroughly cleaned prior to use by washing with detergent, rinsing extensively with tap water followed by high purity deionized water and heating to 560°C for two hours.

Grab samples of ground water to be analyzed for highly volatile organics are usually obtained by means of a Teflon bailer noted in Figure 9.8. Use of the systems described previously is less desirable than bailers for volatile organic samples because of possible stripping of highly volatile constituents from the sample under the reduced or elevated pressure occurring in systems using pumps.

9.6.2.10 Continuous Procedures

Continuous procedures, using selected adsorbents to concentrate and recover organic constituents from relatively large volumes of ground water, may be employed for sampling organic pollutants in situations where the analytical sensitivity and sample uniformity attainable by grab sampling are inadequate. These procedures are applicable for most organic pollutants except those of very high volatility.

A special sampling system is shown in Chapter 12, Figure 12.10 in which the water is pumped directly from the well through Teflon tubing (6 mm O.D.) to two glass columns of adsorbent in series. In this illustration, a peristaltic pump is located on the outlet side of the columns for sampling with suction lift. A noncontaminating submersible pump may be used at greater depths and may be superior for practically all sampling uses. All components of the systems that contact the water sample prior to emergence from the second column are, with the exception of the adsorbent, glass or Teflon.

Columns prepared from macroreticular resins, activated carbon, and polyamide particles are also shown in Chapter 12, Figures 12.7 and 12.8. Of these materials, macroreticular resin (XAD-2, Rohm and Haas Company, Philadelphia, Pennsylvania) has been the most convenient and generally useful and is the current adsorbent of choice.

Sampling is conducted by continuously pumping ground water through the sampling systems at flow rates usually ranging from 10 to 30 mL/min. The volumes sampled are dependent on the desired sensitivity of analysis. For analysis by modern gas chromatographic techniques, sampling of 50 liters of water is sufficient to provide a sensitivity of at least one ug/liter (1 ppb) for almost all compounds of interest. Volumes sampled are determined by measuring the water leaving the sampling systems in calibrated waste receivers.

9.6.2.11 Volatile Organics in the Unsaturated Zone

For investigations pertaining to organic pollution of ground water, it is often desirable to sample water in the unsaturated zone to detect and

follow the movement of pollutants that are migrating toward the water table. This is a particularly difficult task in the case of highly volatile compounds, including the low molecular weight chlorinated hydrocarbons such as trichloroethylene.

Soil water samples may be collected using the device depicted in Figure 9.13, which consists of a sampler, a purging apparatus, and a trap connected to sources of nitrogen gas and vacuum. The soil solution sampler consists of a 7/8 in. O.D. (2.2 cm) porous ceramic cup, a length of 3/4 in. O.D. Teflon or PVC pipe and a Teflon stopper fitted with 3 mm O.D. Teflon exhaust and collection tubes. The length of the pipe is dictated by the depth of sampling desired, which is limited to a maximum of about 20 feet. The device is basically a suction lysimeter and, consequently, suffers from the limitations of such equipment.

The purging apparatus and trap are parts of the Tekmar LSC-1 liquid sample concentrator to which have been added Teflon valves and "Tape-Tite" connectors. The purging apparatus is borosilicate glass, while the trap consists of Tenax GC porous polymer (60/80 mesh), packed in a 2 mm x 28 cm stainless steel tube plugged with silane treated glass wool. The purge gas is ultra high purity, oxygen free nitrogen. Vacuum is provided by a peristaltic pump.

Prior to sample collection, the purging apparatus is cleaned with acetone and distilled water and then baked at 105 to 108°C for at least an hour. In the field, it is rinsed thoroughly with distilled water between samples with special care being exercised to force the rinse water through the glass first.

The soil solution sampler is driven to the bottom of a pre augered 19 mm (0.75 in) diameter hole. This is done very carefully to insure intimate contact between the ceramic cup and the soil.

Prior to collection of a sample, the exhaust tube is opened to the atmosphere and the collection tube disconnected and pumped to remove any solution that may have leaked into the tube through the porous cup. Then, the collection tube is reconnected to the purging apparatus, the exhaust tube closed with a pinch clamp, and 5 to 10 mL of solution is collected by closing valve C and opening valves A and B. After sample collection, the exhaust tube is opened to remove from the sampler and collect on the trap any of the compounds that may have volatilized in the sampler. Following this procedure, A is closed and C opened. Nitrogen gas is then bubbled through the solution at a rate of 40 mL/min for ten minutes to purge volatile organics from solution. Traps are capped and returned to the laboratory for analysis within six hours of collection or for storage at -20°C for later analysis.

Low density, immiscible organics include gasoline and other chemicals and petrochemicals which have specific gravities less than water and which are likely to be present in aquifers as a separate phase because of low solubility in water. These chemicals tend to float on the water surface in a water table environment and commonly occupy the capillary fringe zone

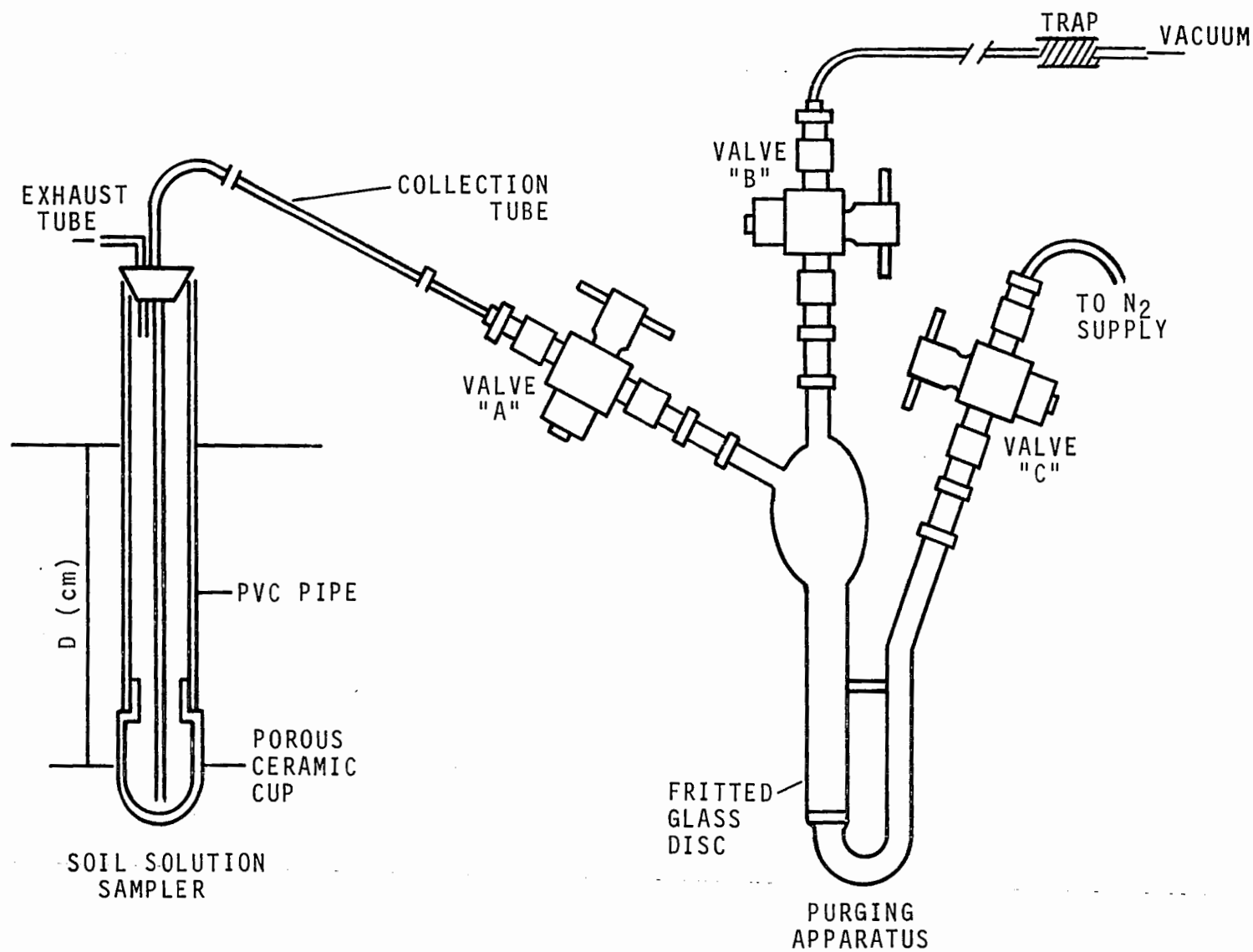


Figure 9.13 Soil-Water Sampling Device for Volatile Organics

above the water table. In a confined aquifer these chemicals are found along the upper surface of the permeable material and also within the overlying confining layer.

Care must be exercised to insure that the well screen extends significantly into both the water saturated zone and the overlying formation. This design will insure that contaminants in the capillary fringe or overlying aquitard, as well as ground water, enter the well to be observed. A well screen with abundant open area such as a wire wrapped screen is important in allowing free flow of the petrochemicals into the well.

With the above considerations in mind, nearly any of the drilling methods which permits a well of at least 3 inches ID to be constructed is satisfactory.

Sampling procedures for low density, immiscible organics differ substantially from those for other pollutants. It is necessary to sample at least two and sometimes three distinct layers of depths within the sampling well.

After the well is initially constructed it should be developed and pumped to remove invaded water, then, it should sit idle for at least several days to allow the water level and floating layer of petrochemicals to fully stabilize.

Measurement of the thickness of the petrochemical layer may then be accomplished by using a water level indicator gel with a steel tape to determine the depth to the water surface. A weighted float may be used to determine the depth to the top of the petrochemical layer. The difference between these two readings is the thickness of the petrochemical layer. Electric water-level sounders will not work properly for these determinations.

A sample of the floating petrochemicals may then be taken using a bailer which fills from the bottom. Care should be taken to lower the bailer just through the petrochemical layer, but not significantly down into the underlying ground water.

Samples of the ground water at the bottom of the screen and at some intermediate location, such as the mid point of the screen, may also be obtained with a bailer. However, in order to avoid mixing the waters, a separate casing is temporarily lowered inside the permanent well casing. This casing is equipped with an easily removed cap on the bottom so that no fluid enters the casing until it has reached the desired depth for sampling. The cap is then knocked free of the bottom of the casing, allowing water to enter from that specific depth to be sampled by bailer. At significant depths below the petrochemicals, several full bailers of water may be withdrawn and discarded before the sample is taken to obtain a fresh formation sample.

9.7. SAMPLING GROUND WATER SUBSURFACE SOLIDS

A common misconception regarding ground water monitoring is that absence of contaminants in the ground water precludes a contamination problem. In many cases, an effective evaluation of the potential impact on ground water quality of activities releasing pollutants into the earth's crust, requires samples of subsurface earth materials, both saturated and unsaturated, as well as ground water samples. There are several principal reasons for this requirement: (a) only by analysis of earth solids from the unsaturated zone underlying pollutant releasing activities can those pollutants which are moving very slowly toward the water table because of sorption and/or physical impediment be detected and their rates of movement and degradation measured. Almost all pollutants are attenuated to some degree in the subsurface, especially in the unsaturated zone. The degree of attenuation and rate of movement varies greatly between different pollutants and different subsurface conditions but many of the mobile pollutants may not be detected in ground water until the activities releasing them have been in operation for protracted periods. Because of their potential for long term pollution of ground water, it is imperative that the behavior of these pollutants in the subsurface be established at the earliest practicable time; (b) analyses of pollutants in subsurface solid samples from the zone of saturation are needed for a realistic evaluation of the total extent and probable longevity of pollution in an aquifer. Such analyses provide a measure of the quantity of pollutants which are sorbed on aquifer solids and which are in equilibrium with, and in essence serve as a reservoir for, pollutants in solution in the adjacent ground water; (c) microbial populations which may be involved in the biological alteration of pollutants in subsurface formations are likely to be in such close association with subsurface solids that they will not be present in well waters in numbers which are quantitatively indicative of their presence in the formations; hence, analysis of subsurface solids are needed for accurate evaluation of such populations and; (d) even when the best well construction and ground water sampling procedures are used, it is difficult to completely eliminate the possibility that contaminating surface microbes may be present in ground water samples. Solids taken from the interior of cores carefully obtained from the zone of saturation probably provide the most authentic samples of aquifer microorganisms that can be obtained.

As with ground water samples, successful sampling of subsurface earth solids requires both acquisition of cores of subsurface solids at desired depths in a manner minimizing potential contamination and proper handling and processing of the core material obtained to insure its integrity and produce samples suitable for analyses.

There are a variety of procedures and equipment that have been used to collect earth materials for classification and identification of physical characteristics. Tools as simple as a shovel or backhoe can and have been used and a number of designed samplers have also been used for this purpose. Because of the ability to penetrate greater depths and to maintain the physical integrity of the samples, most designed samplers employ some type of coring mechanism. The most common procedures use a thin-wall steel tube (core barrel) which is forced into the undisturbed soil at the bottom of a

bore hole. This is sometimes referred to as drive sampling. Core barrels are generally from one inch to three inches in diameter and 12 to 24 inches long. When the core barrel is retrieved, friction will usually retain the sample inside, at least in most unsaturated materials. Additional details on subsurface solid sampling are covered in the Manual of Ground Water Sampling Procedures.(1)

9.8 PRESERVATION AND HANDLING PROCEDURES FOR GROUND WATER PARAMETERS

9.8.1 Organic and Inorganic Parameters

Follow the preservation and handling procedures outlined in Chapter 17 for inorganic and organic parameters.

9.8.2 Microbiological Parameters

There are several different methods for obtaining a ground water sample. Each of these methods differ in their advantages and disadvantages for obtaining samples for microbiological analyses.

The majority of ground water samples are obtained using preexisting wells which have existing in place pumps. This limits the precautions the sampler can take to ensure a non-contaminated sample. Samples should be obtained from outlets as close as possible to the pump and should not be collected from leaky or faulty spigots or spigots that contain screens or aeration devices. The pump should be flushed for 5 to 10 minutes before the sample is collected. A steady flowing water stream at moderate pressure is desirable in order to prevent splashing and dislodging particles in the faucet or water line.

To collect the sample, remove the cap or stopper carefully from the sample bottle. Do not lay the bottle closure down or touch the inside of the closure. Avoid touching the inside of the bottle with your hands or the spigot. The sample bottle should not be rinsed out and it is not necessary to flame the spigot. The bottle should be filled directly to within 2.5 cm (1 inch) from the top. The bottle closure and closure covering should be replaced carefully and the bottle should be placed in a cooler (4 to 10°C) unless the sample is going to be processed immediately in the field.

If a well does not have an existing in-place pump, samples can be obtained by either using a portable surface or submersible pump or by using a bailer. Each method presents special problems in obtaining an uncontaminated sample.

The main problem in using a sterilized bailer is obtaining a representative sample of the aquifer water without pumping or bailing the well beforehand to exchange the water in the bore for fresh formation water. This is difficult since such pre sampling activities must be carried out in such a way as to not contaminate the well. Care must also be taken with bailers to not contaminate the sample with any scum on the surface of the water in the well. This is usually done by using a weighted, sterilized

sample bottle suspended by a nylon rope and lowering the bottle rapidly to the bottom of the well.

The use of portable pumps provides a way of pumping out a well before sampling and thus providing a more representative sample, but presents a potential source of contamination if the pumping apparatus cannot be sterilized beforehand. The method of sterilization will depend on what other samples are taken from the well since the use of many disinfectants may not be feasible if the well is also sampled for chemical analyses. If disinfection is not ruled out by other considerations, a method of sterilizing a submersible pump system is to submerge the pump, and any portion of the pump tubing which will be in contact with the well water, into a disinfectant solution and circulating the disinfectant through the pump and tubing for a recommended period of time.

The most widely used method of disinfection is chlorination due to its simplicity. Chlorine solutions may be easily prepared by dissolving either calcium or sodium hypochlorite in water. Calcium hypochlorite, $\text{Ca}(\text{OCl})_2$, is available in a granular or tablet form usually containing about 70 percent of available chlorine by weight and should be stored under dry and cool conditions. Sodium hypochlorite, NaOCl , is available only in liquid form and can be bought in strengths up to 20% available chlorine. Its most available form is household laundry bleach, which has a strength of about 5% available chlorine, but should not be considered to be full strength if it is more than 60 days old. The original percentage of available chlorine will be on the label.

Table 9.1 gives the quantities of either calcium hypochlorite or laundry bleach required to make 100 gallons of disinfectant solution of various concentrations. Fresh chlorine solutions should frequently be prepared because the strength will diminish with time. The proper strength to use in disinfection is dependent upon many factors including pH and temperature. As a rule of thumb, hypochlorite solutions of 50 to 200 ppm available chlorine and a contact time of 30 minutes should be effective at pH ranges of 6 to 8 and temperatures of greater than 20°C . After disinfection the pump should be carefully placed in the well and then pumped to waste until the chlorine is thoroughly rinsed from the pump system.

TABLE 9.1 QUANTITIES OF CALCIUM HYPOCHLORITE, (70 PERCENT)
AND HOUSEHOLD LAUNDRY BLEACH (5 PERCENT) REQUIRED
TO MAKE 100 GALLONS OF DISINFECTANT SOLUTION

Desired Chlorine Strength	Dry Calcium Hypochlorite, lb.	5% Household Bleach, Quarts
50 ppm	0.07	0.4
100 ppm	.14	0.8
15 ppm	.20	1.2
200 ppm	.30	1.6

If the pump cannot be disinfected, then the pump and tubing should be carefully handled to avoid gross surface contamination and the well should be pumped for 3 to 10 bore volumes before taking a sample. It may be desirable after pumping to pull the pump and take the sample with a sterile bailer.

In those cases where the water level in the well is less than 20 to 30 feet below the surface, a surface vacuum pumping system can be used for flushing out the well and withdrawing a sample. An ideal apparatus for this is depicted in Figure 9.14. This apparatus consists of two lengths of tubing which are sterilizable by autoclaving and portable vacuum system. The two tubing lengths which are attached side-by-side to each other, are sterilized in the laboratory in large covered containers. In the field they are lowered into a well using sterile gloves, attached to a vacuum flask on the inlet side of the pump. Large volume sampling for viruses or pathogenic bacteria can be accomplished by substituting filters or columns with various adsorbents in place of the vacuum flask.

Standing water is prevented from entering the sampling tubing upon insertion into the well by making the sampling tube a few feet shorter than the flushing tubing and turning on the pump to the flushing system as the tubing is put into the well.

To sample wells using this type of system requires a relatively large autoclave, several sets of sampling tubing, and a relatively shallow ground water.

Springs are unlikely to yield representative samples of an aquifer due to surface contamination close to a spring's discharge unless the spring has an extremely fast flow and the outlet is protected from surface contamination.

Lastly, interpretation of analytic results may be difficult in some cases since surface contamination of wells due to poor drilling and completion practices is common. In cases where drinking water supplies are involved, a thorough inspection of the well is required to eliminate surface contamination down the well bore as a source of contaminants. Disinfection of the well by approved methods (9),(10), and resampling may be advisable, if disinfection will not affect the well for other sampling purposes.

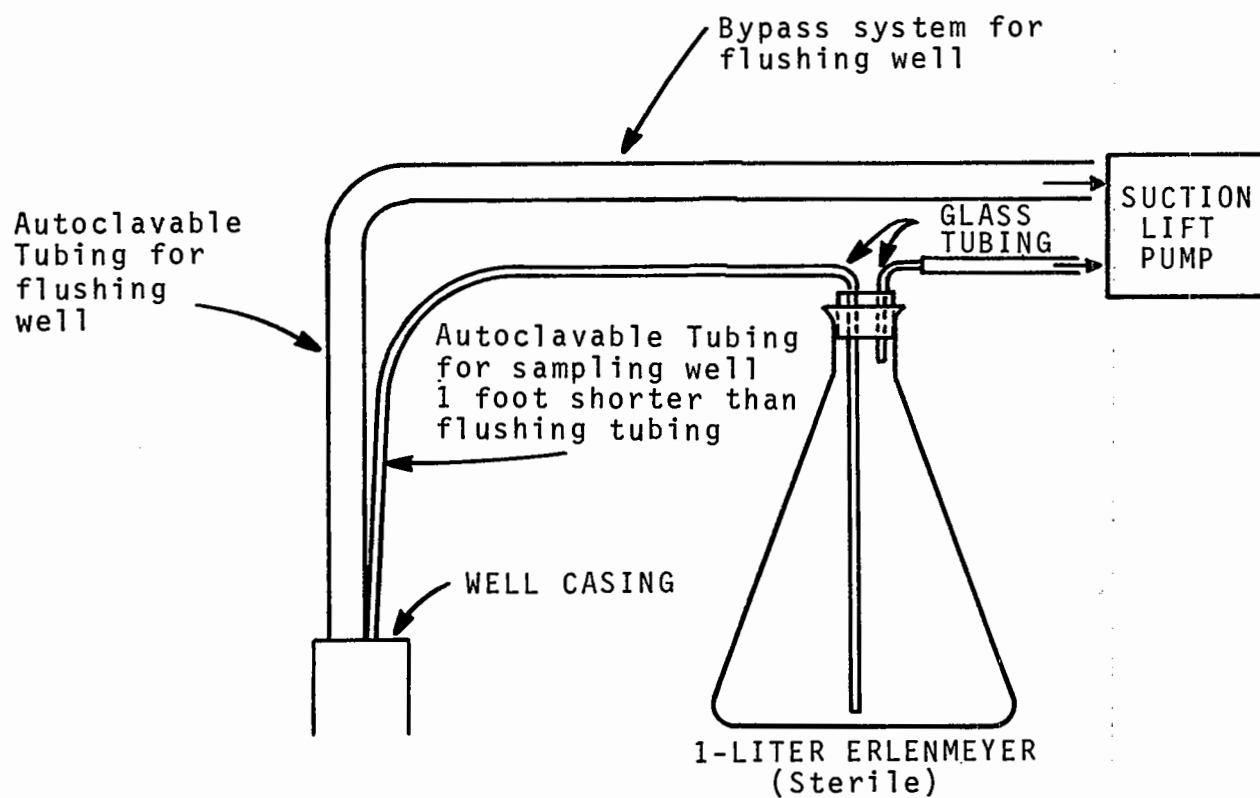


Figure 9.14 System for Microbiological Sampling of Wells Using a Suction-Lift Pump

9.9 SAMPLING OF DRINKING WATER

Under the Safe Water Drinking Act, Public Law 93-523, Section 1412, EPA or states are required to regulate contaminants that may adversely affect public health. Subsequent regulations may require the monitoring of one or more of the following parameters:

PRIMARY DRINKING WATER PARAMETERS

Arsenic	Silver	2,4 D
Barium	Fluoride	2,4,5-TP(Silvex)
Cadmium	Nitrate	Turbidity
Chromium	Endrin	Coliform bacteria
Lead	Lindane	Gross alpha and beta
Mercury	Methoxychlor	Total trihalomethanes
Selenium	Toxaphene	

SECONDARY DRINKING WATER CONTAMINANTS

Copper	Chloride	Color
Manganese	Sulfates	Odor
Iron	pH	Foaming Agents
Zinc	Corrosivity	Total Dissolved Solids

9.9.1 Sampling Location

The sampling locations required by Interim Primary Drinking Regulations for each parameter group are shown in Table 9.2.

The two major considerations in determining the number and location of sampling points are that they should be: 1) Representative of each different water source entering the system, and 2) representative of conditions within the system, such as dead ends, loops, storage facilities and pressure zones.

Examples of selecting sampling points are as follows:(15)

Example 1. One Source to Distribution System

Figure 9.15 demonstrates one source, in this case the clear well effluent, entering the distribution system. Therefore, only one sampling location is needed for such parameters as turbidity and trihalomethanes.

Example 2. One Source to Distribution System

Figure 9.16 demonstrates one source, in this case the treatment plant, entering the distribution system. Therefore, only one sampling location is needed for such parameters as turbidity and trihalomethanes.

TABLE 9.2 SAMPLING LOCATIONS AND FREQUENCIES

What Tests (Community System)	What Tests (Non-Community System)	Sample Location	Frequency (Community System)	How Often (Non-Community System)
Inorganics and SWDC*	Inorganics and SWDC (at state option)	At the consumer's faucet	Systems using surface water: EVERY YEAR Systems using ground water only: EVERY THREE YEARS	All Systems: STATE OPTION
Organics	Organics (at state option)	At the consumer's faucet	Systems using surface water: EVERY THREE YEARS Systems using ground water only: STATE OPTION	All Systems: STATE OPTION
Total Tri- halomethanes	Total Tri- halomethanes	Consumer's tap 25 percent of samples have maximum residence time in system	Systems using surface water: See Figure 9.21	Systems using surface water: See Figure 9.21
MTP	MTP		Systems using surface water: See Figure 9.21	Systems using ground water: See Figure 9.21
Turbidity	Turbidity	At the point(s) where water enters the distribution system	Systems using surface water: DAILY Systems using ground water only: STATE OPTION	Systems using surface or surface and ground water: DAILY Systems using ground water only: STATE OPTION
Coliform Bacteria	Coliform Bacteria	At the consumer's faucet	Depends on number of people served by the water system (See Table 9.1	All Systems: ONE PER QUARTER (for each quarter water is served to public)
Radiochemicals (Natural)	Radiochemicals (Natural) (at state option)	At the consumer's faucet	Systems using surface water: EVERY FOUR YEARS Systems using ground water only: EVERY FOUR YEARS	All Systems: STATE OPTION
Radiochemicals (Man-made)	Radiochemicals (Man-made)- (at state option)	At the consumer's faucet	Systems using surface water serving populations greater than 100,000: EVERY FOUR YEARS All other systems: STATE OPTION	All Systems: STATE OPTION
Sodium	Sodium	At the point(s) where water from each plant enters distribution system	Systems using surface or part surface water ANNUALLY Systems using ground water: EVERY THREE YEARS	All Systems: STATE OPTION
SDWC	SDWC	At the point(s) where water enters the distribution System	All Systems: STATE OPTION	All Systems: STATE OPTION

* Secondary Drinking Water Contaminants

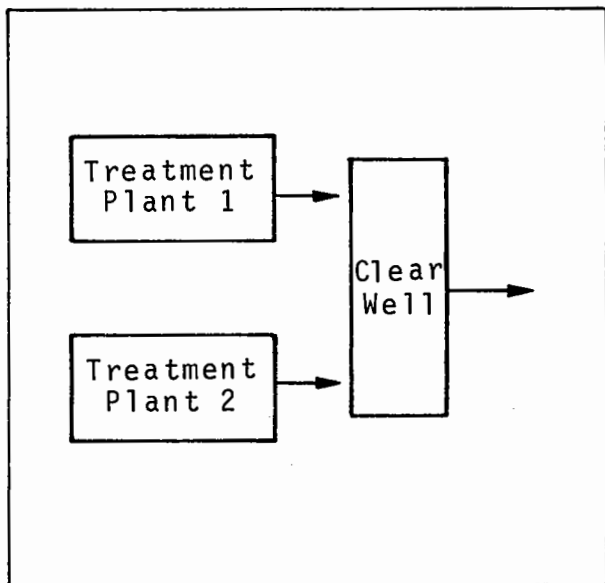


Figure 9.15 One Source Entering Distribution System

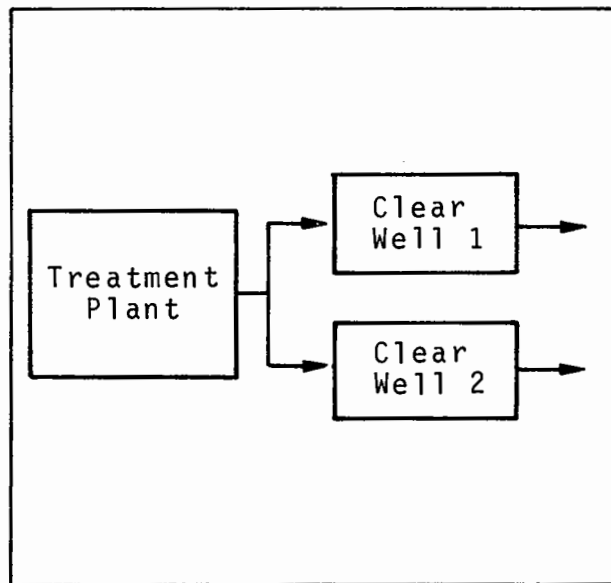


Figure 9.16 Water From One Treatment Plant Entering Two Clear Wells

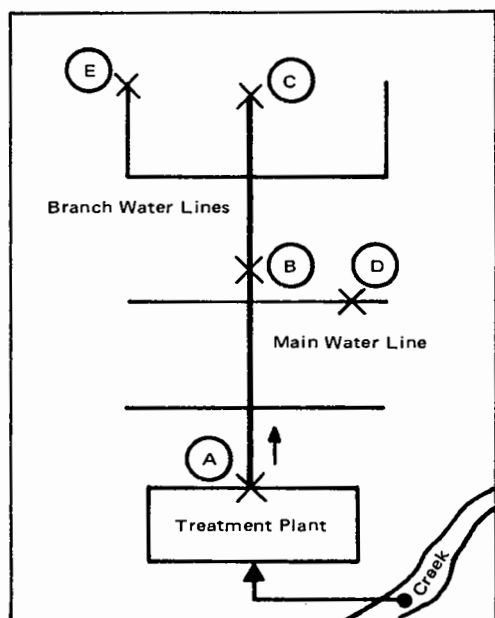


Figure 9.17 Branch Distribution System

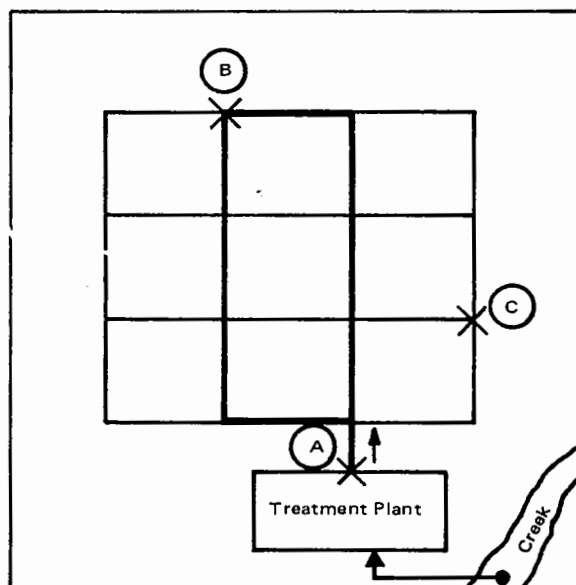


Figure 9.18 Loop Distribution System

Example 3. Conditions Within the System

Figure 9.17 demonstrates sampling locations to determine representative sampling locations in a branch distribution system. Sampling location A is for the entry into the distribution, point B representative of the water in the main line, point C of water in the main dead end, and D and E of water quality in the branch and branch dead end, respectively. Turbidity and trihalomethanes are sampled at point A whereas all others parameters are sampled at points B through D. The frequency of microbiological sampling is proportioned to the population served. For a population of 3500, the required minimum number of samples per month is four. Thus, all four microbiological samples could be taken at the same time from points B, C, D and E. However, representative sampling means representative in time and location. Therefore, sampling should occur at points B and E at mid-month and points C and D at the end of the month.

Example 4. Conditions Within the System

Figure 9.18 demonstrates sampling locations for a Loop distribution system. Sampling location A is for entry into the distribution whereas locations D and C represent water quality in the main line loop and point C in one of the branch line loops.

Example 5. Combined Branch and Loop Systems

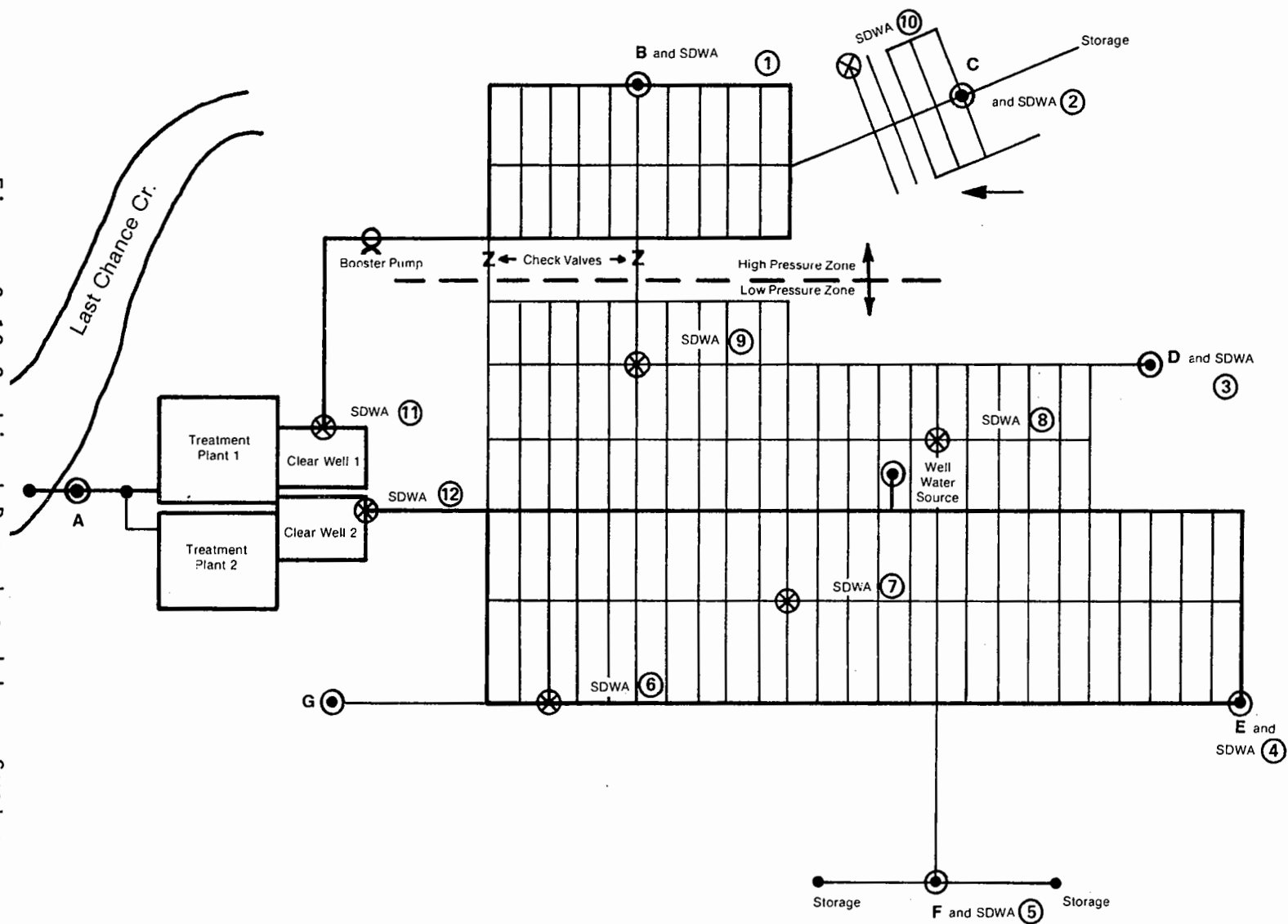
Figure 9.19 demonstrates sampling locations for entry into the distribution system and conditions within a combined branch and loop system. An evaluation of sampling locations follows:

Sampling Point

- A Unacceptable. Point not located in the distribution system or at its entry. Point to be maintained for operational monitoring only.
- B Acceptable. Point on main loop in high-pressure zone; should produce representative samples for that part of system.
- C. Acceptable. Point on branch loop in the high-pressure zone; serves for storage flow to the system.
- D. Judgmental. Many authorities advise against dead end sampling points as they do not produce representative samples. Possibly true; however, consumers do take water from branch-line dead ends. In this example there are seven branch-line dead ends, no doubt serving significant numbers. It would be representative to have one or two sample points on these branch lines at or near the end. (Two in here because of the three source waters and two pressure zones.)

Figure 9.19 Combined Branch and Loop System

259



- E. Acceptable. Located on the main loop of low pressure zone and representing water from treatment plant 2, the well, the storage tanks at F, or any combination. (Depending on system demand at sampling time.)
- F. Judgmental. Although important to sample water quality into system from storage, it might be better to collect the sample at junction of stored water line and main loop, unless consumers are served directly from the storage branch.
- G. Judgmental. Only one dead end need be sampled in low-pressure system. If D selected, A not needed.

Two turbidity sampling points are shown as points 11 and 12, since waters from parallel treatment plants enter two separate clear wells. Notice there is no sampling point where the well water source enters the system since groundwater sources need not be monitored for turbidity.

Sample location is somewhat judgmental, however, general guidelines for selection are:

1. Distribute the Sampling points uniformly throughout the system.
2. Locate the sample points in both types of distribution system configurations: loops and branches and in proportion to the relative number of loops and branches.
3. Locate adequate representative sample points within each zone if there is more than one pressure zone.
4. Locate points so that water coming from storage tanks can be sampled and sample during time of high-demand times.
5. For systems having more than one water source, locate the sample points in relative proportion to the number of people served by each source.
6. Check pressures during the proposed sampling times so that the source of sampled water can be determined. It is possible that excessive demand in one part of the distribution system can cause water to be brought into that area from other parts of the system and perhaps other sources.

9.9.2 Sampling Frequency

Sampling frequencies required by the Interim Primary Drinking Water Regulations (11-14) depend on the parameter group being monitored:

1. Microbiological Sampling - Take coliform bacteria samples at regular time intervals in proportion to the population being served as shown in Table 9.3.

Based on a history of no coliform bacterial contamination and on a sanitary survey by the State showing the water system to be supplied solely by a protected ground water source and free of sanitary defects, a community water system serving 25 to 1,000 persons, with written permission from the State, may reduce this

Table 9.3 FREQUENCY OF MICROBIOLOGICAL SAMPLING

Population Served	Min. No. of Samples per Month	Population Served	Min. No. of Samples per Month
25 to 1,000	1	90,000 to 96,000	95
1,001 to 2,500	2	96,001 to 111,000	100
2,501 to 3,300	3	111,001 to 130,000	110
3,301 to 4,100	4	130,001 to 160,000	120
4,101 to 4,900	5	160,001 to 190,000	130
4,901 to 5,800	6	190,001 to 220,000	140
5,801 to 6,700	7	220,001 to 250,000	150
6,701 to 7,600	8	250,001 to 290,000	160
7,601 to 8,500	9	290,001 to 320,000	170
8,501 to 9,400	10	320,001 to 360,000	180
9,401 to 10,300	11	360,001 to 410,000	190
10,301 to 11,100	12	410,001 to 450,000	200
11,101 to 12,000	13	450,001 to 500,000	210
12,001 to 12,900	14	500,001 to 550,000	220
12,901 to 13,700	15	550,001 to 600,000	230
13,701 to 14,600	16	600,001 to 660,000	240
14,601 to 15,500	17	660,001 to 720,000	250
15,501 to 16,300	18	720,001 to 780,000	260
16,301 to 17,200	19	780,001 to 840,000	270
17,201 to 18,000	20	840,001 to 910,000	280
18,001 to 18,900	21	910,001 to 970,000	290
18,901 to 19,800	22	970,001 to 1,050,000	300
19,801 to 20,700	23	1,050,001 to 1,140,000	310
20,701 to 21,500	24	1,140,001 to 1,230,000	320
21,501 to 22,300	25	1,230,001 to 1,320,000	330
22,301 to 23,200	26	1,320,001 to 1,420,000	340
23,201 to 24,000	27	1,420,001 to 1,520,000	350
24,001 to 24,900	28	1,520,001 to 1,630,000	360
24,901 to 25,000	29	1,630,001 to 1,730,000	370
25,001 to 28,000	30	1,730,001 to 1,850,000	380
28,001 to 33,000	35	1,850,001 to 1,970,000	390
33,001 to 37,000	40	1,970,001 to 2,060,000	400
37,001 to 41,000	45	2,060,001 to 2,270,000	410
41,001 to 46,000	50	2,270,001 to 2,510,000	420
46,001 to 50,000	55	2,510,001 to 2,750,000	430
50,001 to 54,000	60	2,750,001 to 3,020,000	440
54,001 to 59,000	65	3,020,001 to 3,320,000	450
59,001 to 64,000	70	3,320,001 to 3,620,000	460
64,001 to 70,000	75	3,620,001 to 3,960,000	470
70,001 to 76,000	80	3,960,001 to 4,310,000	480
76,001 to 83,000	85	4,310,001 to 4,690,000	490
83,001 to 90,000	90	4,690,001 or more	500

sampling frequency except that in no case shall it be reduced to less than one per quarter. The supplier of water for a non-community water system shall sample for coliform bacteria in each calendar quarter during which the system provides water to the public. If the State, on the basis of a sanitary survey, determines that some other frequency is more appropriate, that frequency shall be the frequency required. Such frequency may be confirmed or changed on the basis of subsequent surveys.

When the coliform bacteria in a single sample exceed four per 100 milliliters, at least two consecutive daily check samples shall be collected and examined from the same sampling point. Additional check samples shall be collected daily, or at a frequency established by the State, until the results obtained from at least two consecutive check samples show less than one coliform bacterium per 100 milliliters. When coliform bacteria occur in three or more 10 mL portions of a single sample, at least two consecutive daily check samples shall be collected and examined from the same sampling point. Additional check samples shall be collected daily, or at a frequency established by the State, until the results obtained from at least two consecutive check samples show no positive tubes.

When coliform bacteria occur in all five of the 100 mL portions of a single sample, at least two daily check samples shall be collected and examined from the same sampling point. Additional check samples shall be collected daily, or at a frequency established by the State, until the results obtained from at least two consecutive check samples show no positive tubes.

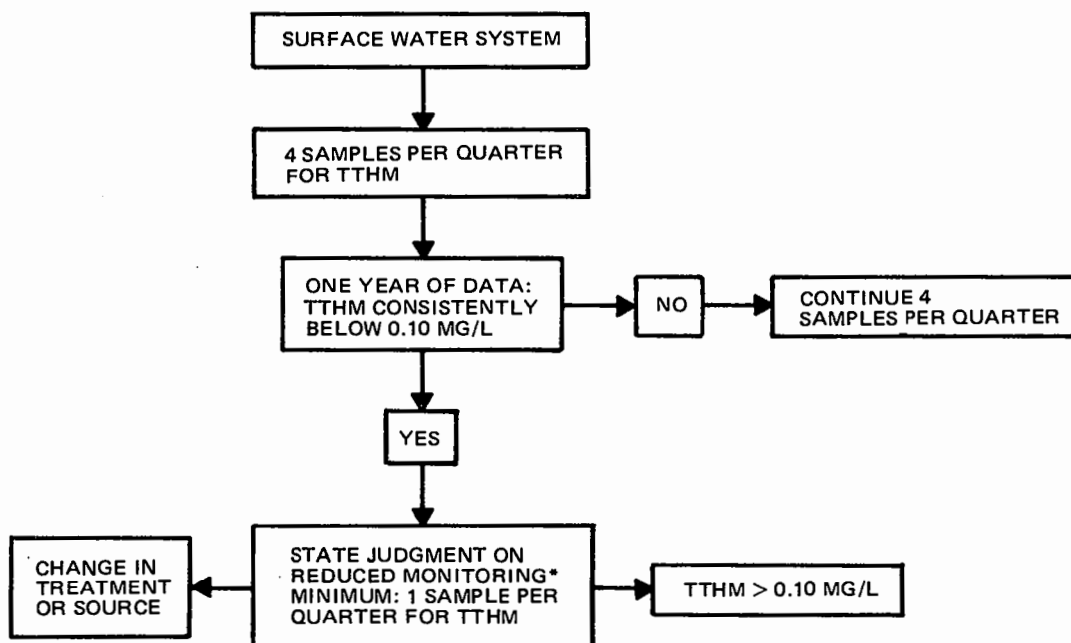
2. Other Parameter Groups - See table 9.2, Sampling Locations and Frequencies.
3. Total Trihalomethanes - See Figures 9.20 and 9.21.

9.9.3 Representative Samples

Follow the procedures specified below to assure the collection of a representative sample and to maintain the integrity of the sample:

1. Collect samples at faucets which are free of contaminating devices such as screens, aeration devices, hoses, purification devices or swiveled faucets. Check faucet to be sure it is clean; if the faucet is in a state of desrepair, select another sampling location.
2. Collect samples in areas free of excessive dust, rain, snow or other sources of contamination.
3. Collect samples from faucets which are high enough to put a bottle underneath, generally the bath tub, without contacting the mouth of the container with the faucet.
4. Open faucet and thoroughly flush. Generally 2 to 3 minutes will suffice, however longer times may be needed, especially in the case of lead distribution lines. Generally, the water temperature will

THE MINIMUM MONITORING REQUIREMENT IS FOUR SAMPLES PER QUARTER PER PLANT. REDUCED MONITORING REQUIREMENTS MAY BE APPROPRIATE IN CERTAIN CASES; UPON WRITTEN REQUEST FROM THE PUBLIC WATER SYSTEM, STATES MAY REDUCE THE REQUIREMENTS THROUGH CONSIDERATION OF APPROPRIATE DATA AS FOLLOWS:

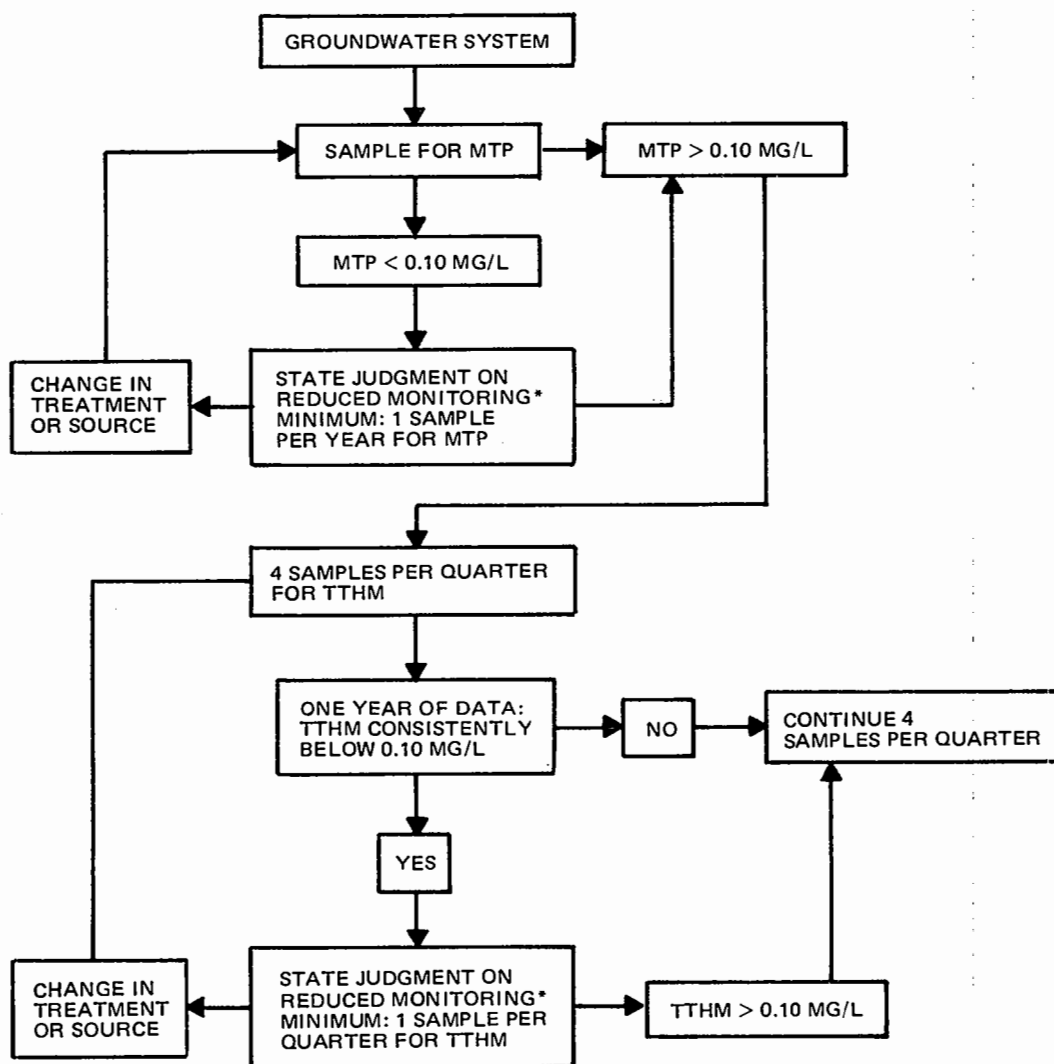


*FACTORS FOR CONSIDERATION:

- MONITORING DATA, MTP, TTHM, TOC
- QUALITY AND STABILITY OF SOURCE WATER
- TYPE OF TREATMENT

Figure 9.20 Total trihalomethanes sampling frequency for surface water systems

THE MINIMUM MONITORING REQUIREMENT IS FOUR SAMPLES PER QUARTER PER PLANT; SYSTEMS USING MULTIPLE WELLS DRAWING RAW WATER FROM A SINGLE AQUIFER MAY WITH STATE APPROVAL BE CONSIDERED AS ONE TREATMENT PLANT. REDUCED MONITORING REQUIREMENTS MAY BE APPROPRIATE IN CERTAIN CASES; UPON WRITTEN REQUEST FROM THE PUBLIC WATER SYSTEM, STATES MAY REDUCE THE REQUIREMENTS THROUGH CONSIDERATION OF APPROPRIATE DATA AS FOLLOWS:



*FACTORS FOR CONSIDERATION:

- MONITORING DATA, MTP, TTHM, TOC
- QUALITY AND STABILITY OF SOURCE WATER
- TYPE OF TREATMENT

Figure 9.21 Total trihalomethanes sampling frequency for ground water systems

TABLE 9.4 PRESERVATION AND HOLDING TIMES FOR SDW PARAMETERS

Parameter	Preservative ^{1,2}	Container ³	Maximum ^{1,4} Holding Time
Arsenic	Conc HNO ₃ to pH 2	P or G	6 months
Barium	Conc HNO ₃ to pH 2	P or G	6 months
Cadmium	Conc HNO ₃ to pH 2	P or G	6 months
Chromium	Conc HNO ₃ to pH 2	P or G	6 months
Lead	Conc HNO ₃ to pH 2	P or G	6 months
Mercury	Conc HNO ₃ to pH 2	G P	38 days 14 days
Nitrate	Conc H ₂ SO ₄ to pH 2	P or G	14 days
Selenium	Conc HNO ₃ to pH 2	P or G	6 months
Silver	Conc HNO ₃ to pH 2	P or G	6 months
Fluoride	None	P or G	1 month ⁵
Chlorinated hydrocarbons	Refrigerate at 4°C as soon as possible after collection	G with foil or Teflon-lined cap	14 days ⁵
Chlorophenoxys	Refrigerate at 4°C as soon as possible after collection	G with foil or Teflon-lined cap	7 days
Fecal Coliform	Refrigerate at 4°C as soon as possible after collection	Sterile P or G	30 hours
TTHM's	See Chapter 17		
Residual Chlorine	None	P or G	1 hour
Turbidity	None	P or G	1 hour

¹If a laboratory has no control over these factors, the laboratory director must reject any samples not meeting these criteria and so notify the authority requesting the analyses.

²If HNO₃ cannot be used because of shipping restrictions, sample may be initially preserved by icing and immediately shipping it to the laboratory. Upon receipt in the laboratory, the sample must be acidified with conc HNO₃ to pH 2. At time of analysis, sample container should be thoroughly rinsed with 1:1 HNO₃; washings should be added to sample.

³P = Plastic, hard or soft; G = Glass, hard or soft.

⁴In all cases, samples should be analyzed as soon after collection as possible.

⁵Well-stoppered and refrigerated extracts can be held up to 30 days.

TABLE 9.5 PRESERVATION AND HOLDING TIMES FOR SDW RADIOLOGICAL PARAMETERS

Parameter	Preservative ²	Instru- ^{1,4} mentation
Gross alpha	Concl.HCl or HNO ₃ to pH 2 ⁵	P or G A or B
Gross beta	Concl.HCl or HNO ₃ to pH 2 ⁵	P or G A
Strontium-89	Concl.HCl or HNO ₃ to pH 2	P or G A
Strontium-90	Concl.HCl or HNO ₃ to pH 2	P or G A
Radium-226	Concl.HCl or HNO ₃ to pH 2	P or G A, B, or D
Radium-228	Concl.HCl or HNO ₃ to pH 2	P or G A
Cesium-134	Concl.HCl to pH 2	P or G A or C
Iodine-131	None	P or G A
Tritium	None	G E
Uranium	Concl.HCl or HNO ₃ to pH 2	P or G F
Photon emitters	Concl.HCl or HNO ₃ to pH 2	P or G C

¹FEDERAL REGISTER Vol. 41 No. 133 July 9 1976

²It is recommended that the preservative be added to the sample at the time of collection unless suspended solids activity is to be measured. However, if the sample must be shipped to a laboratory or storage area, acidification of the sample (in its original container) may be delayed for a period not to exceed 5 days. A minimum of 16 hours must elapse between acidification and analysis.

³P = Plastic, hard or soft; G = Glass, hard or soft.

⁴A = Low background proportional system; B = Alpha scintillation system; C = Gamma spectrometer (NaI(Tl) or GE(Li)); D = Scintillation cell (radon) system; E = Liquid scintillation system (section C.2.a); F = Fluorometer (section C.1.i).

⁵If HCl is used to acidify samples which are to be analyzed from gross alpha or gross beta activities, the acid salts must be converted to nitrate salts before transfer of the samples to planchets.

stabilize which indicates flushing is completed, then adjust the flows so it does not splash against the walls of bathtubs, sinks or other surfaces. Collect samples.

5. Collect microbiological samples with sterile containers and caps. Handle container caps aseptically, i.e. hold the cap in one hand without touching the inner surface while sampling. It is not necessary to flame the faucet, however faucets in good repair must be flushed thoroughly before microbiological sampling.
6. For most samples, fill container to one to one and one half inches from the top. For Trihalomethanes and other organics, follow procedures specified in Chapter 12.
7. Handle, preserve, and adhere to holding times between sampling and analyses as shown in Tables 9.4 and 9.5: (4)
8. Identify sample immediately after collection using an appropriate numbering system. Identification includes such written information (non-smearing ink) as water source, location, time and date of collection, and collectors name. Record chlorine residual if applicable.
9. Record above data and any additional remarks in a field notebook.

9.10 REFERENCES

1. Marion, R., D. Scalf, J.F. McNabb W.J. Dunlap R.L. Cosby and J.S. Fryberger. Manual of Ground Water Quality Sampling Procedures. Robert S. Kerr Environmental Research Lab, Office of Research and Development, U.S. Environmental Protection Agency, Ada, Oklahoma, May 1980.
2. Procedures Manual for Ground Water Monitoring at Solid Waste Disposal Facilities. U.S. Environmental Protection Agency. EPA 530/SW-611. August, 1977.
3. Keys, W.S. and L.M. MacCary. Application of Borehole Geophysics to Water Resources Investigations. U.S. Geological Survey Techniques of Water Resource Investigations. Book 2 Chapter E-1 pp. 1-126. 1971.
4. Bianchi, W.C. C.E. Johnson and E.E. Haskell. A Positive Action Pump for Sampling Small Bore Wells. Soil Science Society of America. Proceedings, Vol. 26. No.1. 1962.
5. Smith, A.J. Water Sampling Made Easier with New Device. The Johnson Drillers Journal. July-August, 1976.
6. Signor, D.C. Gas Driven Pump for Ground Water Samples. U.S.G.S. Water Resources Investigation. 78-72 Open file report. July, 1978.
7. Minning, R.C. Keck Consulting Services, Inc. Private Communication. 1980.
8. Dunlap, W.J. J.F. McNabb M.R. Scalf and R.L. Cosby. Sampling for Organic Chemicals and Microorganisms in the Subsurface. EPA - 600/2-77-176. August, 1977.

9. Cambell, M.D. and J.H. Lehr. Water Well Technology. McGraw Hill Book Company. New York. 1973.
10. Manual of Individual Water Supply Systems. EPA - 430/9-74-007. USEPA OWP. Washington. 1974.
11. Environmental Protection Agency. Office of Water Supply. National Interim Primary Drinking Water Regulations. EPA-570/9-76-003. July 1976.
12. Environmetnal Protection Agency. Interim Primary Drinking Water Regulations-Control of Organic Chemical Contaminants in Drinking Water. Federal Register 40 CFR part 141 volume 43 No.28 February 9 1978.
13. Environmental Protection Agency. Interim Primary Drinking Water Regulations-Amendments. Federal Register, 40 CFR part 141 Volume 45 No.168 August 27 1980.
14. Environmental Protection Agency. Manual For The Interim Certification Of Laboratories Involved In Analyzing Public Drinking Water Supplies. EPA 600/8-78-008. May 1978.
15. American Water Works Association. The Safe Water Drinking Act - Handbook for Water System Operators. Report Number IP-10M-1/78-1612.

CHAPTER 10

SAMPLING SLUDGES

10.1 BACKGROUND

The quantity and composition of sludge varies with the characteristics of the wastewater from which it is concentrated and with the concentration process used. Some common types of sludge are:

1. Coarse screenings from bar racks
2. Grit
3. Scum from primary settling tanks
4. Primary settling tank sludge
5. Return and waste activated sludge
6. Floatation or gravity thickened sludge
7. Aerobic or anaerobic digester sludge
8. Drying bed sludge
9. Vacuum filter cake
10. Sludge press cake
11. Centrifuge sludge
12. Fine screening backwash water
13. Sand filter backwash water
14. Sludges from special treatment processes such as the treatment of industrial wastes or combined sewer overflows.

Sludge sampling methods are usually confined to municipal or industrial plants. The sampling programs employed are concerned mainly with the following sludges: primary settling tank sludge, return and waste activated sludge, thickened sludge, digester sludge, and the resulting cakes produced by sludge drying methods.

10.2 OBJECTIVES OF SAMPLING PROGRAMS

10.2.1 Process Control

Most sludges are measured for the following process control reasons:

1. Optimization of sludge drawoff procedure
2. Determination of the efficiency of a concentration process
3. Determination of the loadings to the process
4. Evaluation of feed material for subsequent sludge conditioning techniques which may vary with changing feed characteristics
5. Control of the activated sludge process, i.e., the mixed liquor

- suspended solids (MLSS) concentration
- 6. Control of blanket depths in clarifiers
- 7. Determination of sludge characteristics that may be detrimental to digester processes

10.2.2 Research

Research projects require specific sampling techniques which are determined by the program.

10.3 PARAMETERS TO ANALYZE

The parameters to analyze will depend on the objective of the process. For example, analysis of total and suspended solids content of the sludge is necessary to determine the efficiency of a sludge thickening process. A guide for parameters to analyze is shown in Figure 10.1. Additional parameters to analyze include: heavy metals, pesticides, and nutrients.

10.4 LOCATION OF SAMPLING POINTS

10.4.1 Flowing Sludges

10.4.1.1 Piping

Collect samples directly from the piping through a sampling cock having a minimum I.D. of 3.8 cm (1.5 inches). (1)

10.4.1.2 Channels

Collect samples at the measuring weirs, or at another point where the sludge is well mixed.

10.4.2 Batch Sludges

10.4.2.1 Digesters

Collect samples from a mixed sink which is fed through lines attached at different levels in the digester. Be certain to waste sludge accumulated in the lines prior to sampling. (1)

10.4.2.2 Tanks

Mix tank thoroughly and collect samples. Collect samples at various depths and locations in the tank. Mix samples together prior to analysis.

10.4.3 Specific "In Plant" Locations

The following locations are recommended for sludge sampling at wastewater treatment plants:

	Gravity Thickening		Air Flotation Thickening		Centrifugation		Vacuum (presure) Filtration		Aerobic Digestion		Anaerobic Digestion Primary		Anaerobic Digestion Secondary		Wet Air Oxidation	
	F ¹	L ²	F	L	F	L	F	L	F	L	F	L	F	L	F	L
Temperature									1/D	1s	Mn	1s	Mn	1s	Mn	1s
pH									1/D	1s	1/D	1s			1/D	S
BOD	2/W	Su	2/W	Su	1/W	C	2/W	F	AD	S			1/W	S	2/D	S
SS	1/D	Su	1/D	Su	1/D	C	1/D	F	AD	S			1/W	S	1/D	S
TS	1/D	1 P	1/D	1 P	1/D	1 P	1/D	1 P	2/W	1 P	1/W	1s	AD	U	1/D	1 U
TVS									2/W	1 P	1/W	1s	AD	U		
Alkalinity											1/D	1s				
Volatile Acids											2/W	1				
Settleable Solids					1/H	C			3/W	1s						

1. F = frequency
2. L = location

Where:

Mn = monitor
H = hour
D = day
W = week

AD = at drawoff
Su = supernatant
I = influent
P = product sludge or cake
C = centrate
F = filtrate
Is = in situ
S = supernatant or decant
U = underflow

Figure 10.1 Recommended minimum sampling programs for municipal wastewater sludge treatment processes (2)

1. Primary Sludge - Draw sludge from the settling tank hoppers into a well or pit before pumping, mix well and then collect a representative sample directly from this well. Alternately, collect samples from openings in pipes near the sludge pumps or from the pump itself. (3)
2. Activated Sludge - Collect samples at:
 - a. the pump suction well
 - b. the pump or adjacent piping
 - c. the point of discharge of the return sludge to the primary effluent.

The sample point should be located in a region of good agitation to the suspension of solids. (3)

3. Digested Sludge - Collect samples at the point of the discharge of the digester drawoff pipe to the drying beds or the drying equipment. (4)
4. Bed Dried Sludge - Collect equal sized samples at several points within the bed without including sand. Mix thoroughly. (3)
5. Filtered Sludge - Collect equal size portions (possibly by using a cookie cutter) at the filter discharge. (3)

10.5 FREQUENCY OF SAMPLING

The extreme variability of sludges creates a need for frequent sampling to achieve accurate results. Each composite sample should be composed of at least 3 individually obtained samples. (3) Sample batch operations at the beginning, middle and end of a discharge, or more frequently if high variability is suspected. (3) Tapped lines should also be sampled in three separate intervals because of variations in the sludge at the drawoff source (i.e., clarifier, digester, etc.). Minimum frequencies for various sludge processes are included in Figure 10.1

10.6 NUMBER OF SAMPLES

The number of samples is determined from the frequency and the number to include in the composite. Refer to Figure 10.1 for minimum guidelines.

10.7 TYPE OF SAMPLE

Collect grab samples when analyzing for a parameter which is unstable, for example ammonia, or when analysis is required as soon as possible (for example, sludge volume index test for activated sludge samples).

Analysis of composite samples is recommended in all other situations to reduce the effects of sludge variability. Use at least three individual samples to form the composite. Wherever possible, collect frequent discrete samples and composite according to flow rate. (5)

10.8 METHOD OF SAMPLING

Automatic samplers are not commonly available for sludge sampling due to the high fouling potential and solids content of the wastewater. Use manual sampling techniques in most situations unless special adaptations can be made.

10.9 VOLUME OF SAMPLE AND CONTAINER TYPE

Use a wide mouth container to sample sludges. The size and material of container depends on the parameters to be analyzed. In general, a clean borosilicate glass container is preferable to reduce the possibility of adsorption of organics to the container wall; however, polyethylene can be used for inorganic analyses. See Chapter 17 for more details.

10.10 PRESERVATION AND HANDLING OF SAMPLES

Preservation methods are discussed in Chapter 17. Completely mix the sample after a preservative is added to disperse the chemical for adequate preservation. Considerable mixing or homogenization is required prior to aliquot removal to insure representative portions are obtained.

10.11 FLOW MEASUREMENT

For flowing lines do not use flow measuring devices which will be easily fouled by solids (for example, orifice, venturi meter). Use a permanently installed self-cleaning or non-obstructive device such as a magnetic flow meter.

Batch sludge discharges are not easily quantified in terms of volume discharged. Make estimates from pump capacity, the change in depth in a tank or well and time of pumping or other appropriate methods.

10.12 REFERENCES

1. Joint Committee of American Society of Civil Engineers and Water Pollution Control Federation. Sewage Treatment Plant Design - WPCF Manual of Practice, No 8, 1967.
2. Estimating Laboratory Needs for Municipal Wastewater Treatment Plants. U.S. EPA, Office of Water Program Operations, Washington, D.C., Report No. EPA 430/9-74-002. Operation and Maintenance Program. June 1973, pp. A-1 to A-29.
3. New York State Department of Health. Manual of Instruction for Sewage Treatment Plant Operators, New York, New York, Health Education Service, 308 p.

4. Technical Practice Committee - Subcommittee on Operation of Wastewater Treatment Plants. Operation of Wastewater Treatment Plant - WPCF Manual of Practice No. 11, 1970.
5. Technical Practice Committee - Subcommittee on Sludge Dewatering, Sludge Dewatering - WPCF Manual of Practice No. 20, 1969.

CHAPTER 11

SUSPENDED SOLIDS SAMPLING

Suspended solids are a key water quality parameter since they impact such activities as the design of wastewater treatment plants, turbidity removal in drinking water, sediment control in streams, and disinfection. The concentration of other water quality parameters is related to suspended solids, since the solid structure may contain biochemical and chemical oxygen demand materials, trace metals, nutrients, pesticides and toxic or hazardous materials adsorbed on the surface.

11.1 REPRESENTATIVE SAMPLING THEORY

For solids distributed uniformly within a given system and containing the same chemical and physical properties, any sample taken shall be representative. However, most systems in practice contain suspended solids varying in physical and/or chemical properties; in practice, the degree of non-uniformity ranges from slight to large and subsequently causes problems in obtaining a representative sample.

11.1.1 Sampling Error

The error in sampling suspended solids in the field or subsampling from a previously collected sample is attributed to two factors: 1) solid segregation effects; and 2) random distribution of solids:

- a) Segregation Effects - Error in sampling due to significant differences between solid particles in specific gravity, size, and shape.
- b) Random Solid Distribution - Error due to imperfect sampling or homogenization procedures. For example, a mixture of 1,000 green beads and 5,000 yellow beads, color being the only difference, is homogenized as completely as possible. However, a sample of 24 beads will not always contain four green beads but may vary from zero to eight. The magnitude of this type of error depends on the size of the sample being withdrawn.

Segregation effects are more pronounced in field sampling since solids are difficult to mix thoroughly or process through devices that eliminate solid segregation. Random effects are more pronounced in the laboratory since segregation effects can be minimized by homogenization of the wastewater sample.

11.2 SEGREGATION SAMPLING ERROR

Typical waters/wastewaters contain solid particles which vary in size, shape, and specific gravity. These properties influence the particle settling rate which must be exceeded to keep the solid suspended and prevent segregation of solids within the water/wastewater system being sampled. The theoretical settling rate of a spherical solid in a quiescent aqueous medium is given by Stokes' Law:

$$V_s = \frac{D^2(S_s - S_w)g}{18 \nu}$$

Where: V_s = settling velocity

D = sphere diameter

S_s = specific gravity of solid

S_w = specific gravity of water

ν = kinematic viscosity of water

g = acceleration of gravity

11.2.1 Particle Size

Stokes' Law indicates that the settling velocity increases with increasing particle diameter. The size of solids found in water/wastewater varies as shown in Figure 11.1. Approximately 90% of all solids are less than 1 mm in size.

11.2.2 Specific Gravity of Solids

Stokes' Law also indicates that the settling rate increases with increasing specific gravity of the solid. The specific gravity of suspended solids found in waters/wastewaters varies from 0.8 to 3.5, examples are shown below:

<u>Material</u>	<u>Specific Gravity</u>
Oils, other organics	0.95
Flocculated mud particles with 95% water	1.03
Municipal	
a) Effluents	1.15
b) Influent	0.8 - 1.6
c) Grit	1.2 - 1.7
Aluminum Floc	1.18
Iron Floc	1.34
Sand	2.65
Calcium Carbonate Precipitate	2.70

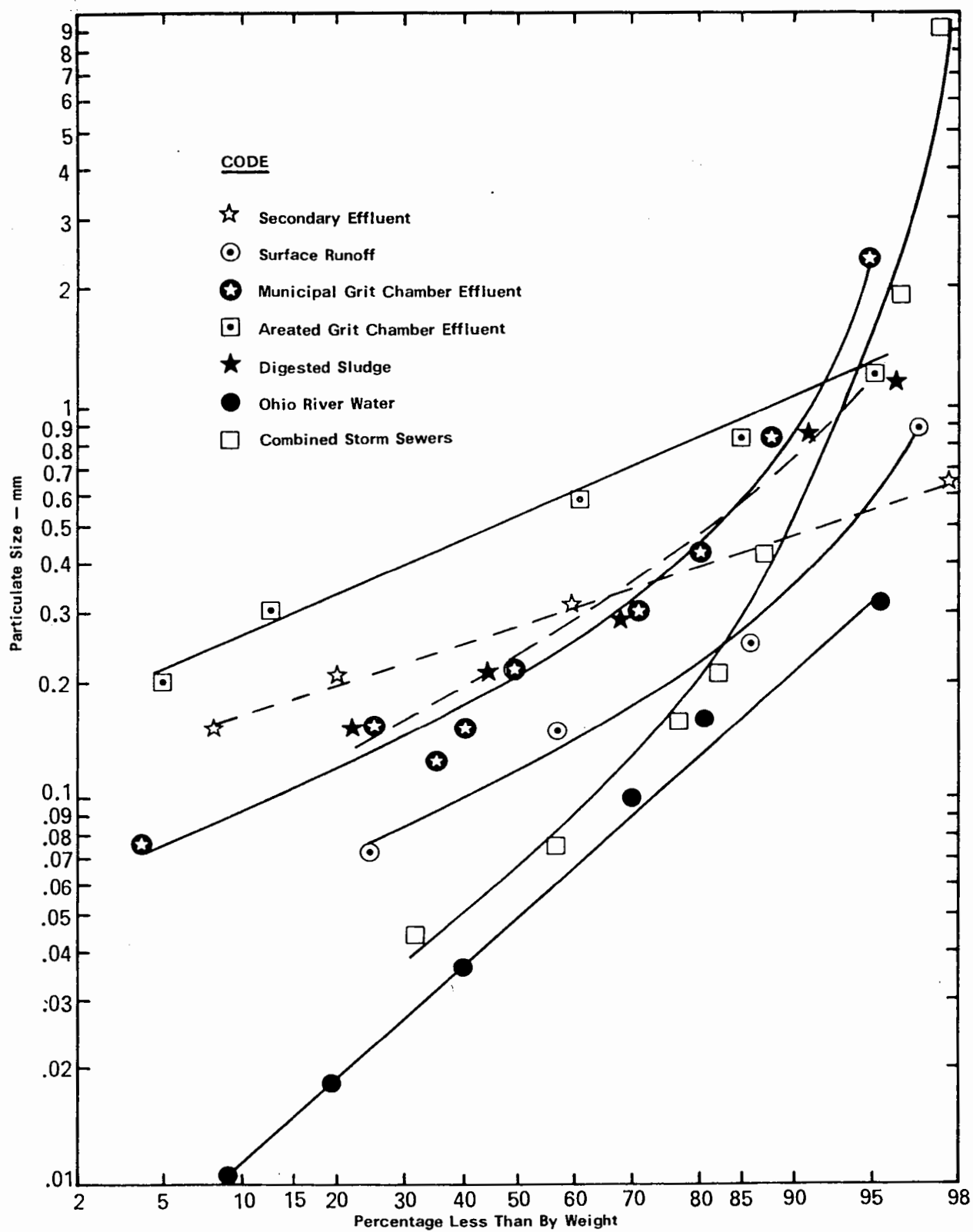


Figure 11.1 Suspended solid particle sizes in various waters/waste waters (1).

11.2.3 Shape of Solids

The settling velocity formula of Stokes applies to spherical particles, however, most waters/wastewaters contain solids of non-spherical shape. In general solids with irregular shapes settle at lower rates than spherical particles of the same specific gravity.(2) Shapes encountered in waters/wastewaters include:

<u>Type</u>	<u>Shape</u>
a) Microbiological and paper scraps	Placoid
b) Sand grains	Angular
c) Plastic monomers	Spherical
d) Fibers - wood, rayon, nylon	Cylindrical-stringy

11.2.4 Settling Velocities

Experimentally determined settling velocities (1) for various solid types are:

- a) Erosion soil run-off - Ranges from .015 - 10.1 cm/sec (.0005 - 0.33 ft/sec).
- b) Grit chamber effluent - Mean of 0.54 cm/sec (.0017 ft/sec).
- c) Primary clarifier design for settable solids removal - .028 - .043 cm/sec (.0009 - .0014 ft/sec).

11.2.5 Scouring Velocity

Sampling of horizontal flowing open channels and pipes for suspended solids must be conducted at velocities which assures adequate mixing. Stratification or segregation of solids are classified as follows:

- a) Bed load - Solids that move by saltation, rolling, or sliding along or near the bottom surface.
- b) Suspended solids or suspended load - solids that are supported by the upward components of turbulent currents and that they stay in suspension for appreciable amounts of time. The equation for estimating the velocity (3) to transport solids is:

$$V_s = \frac{8B}{f} (g) (S - 1) Dg = \frac{1.486}{n} R^{1/6} B (S - 1) Dg$$

Where:

V_s = Scouring velocity

S = Specific gravity of the particle

Dg = Diameter of particle

B = 0.04 to start scouring and 0.8 for scouring

f = Friction factor - .03 for concrete

n = Manning roughness factor - See Table 11.1

R = Hydraulic Radius - See Table 11.2

g = 32.2 ft/sec².

TABLE 11.1 VALUES OF MANNING'S ROUGHNESS COEFFICIENT n

Glass, plastic, machined metal	0.010
Dressed timber, joints flush	0.011
Sawn timber, joints uneven	0.014
Cement plaster	0.011
Concrete, steel troweled	0.012
Concrete, timber forms, unfinished	0.014
Untreated gunite	0.015 - 0.017
Brick work or dressed masonry	0.014
Rubble set in cement	0.017
Earth, smooth, no weeds	0.020
Earth, some stones and weeds	0.025
Natural river channels:	
Clean and straight	0.025 - 0.030
Winding, with pools and shoals	0.033 - 0.040
Very weedy, winding and overgrown	0.074 - 0.150
Clean straight alluvial channels	$0.031d^{1/6}$ d D-75 size in ft.

TABLE 11.2 VALUES OF HYDRAULIC RADIUS R_H FOR VARIOUS CROSS SECTIONS

$$R_H = \frac{\text{area of stream cross section}}{\text{wetted perimeter}}; \text{ "equivalent diameter" } = 4R_H$$

Shape of Cross Section	R_H
Pipes and ducts, running full:	
Circle, diam. = D	$\frac{D}{4}$
Annulus, inner diam. = d. outer diam. = D	$\frac{(D - d)}{4}$
Square, side = D	$\frac{D}{4}$

(continued)

TABLE 11.2 (continued)

Shape of Cross Section	R_H
Rectangle, sides a, b	$\frac{ab}{2(a + b)}$
Ellipse, major axis = 2a, minor axis = 2b	$\frac{ab}{K(a + b)^*}$
Open channels or partly filled ducts:	
Rectangle, depth = y, width = b	$\frac{by}{b + 2y}$
Semicircle, free surface on a diam. D	$\frac{D}{4}$
Wide shallow stream on flat plate, depth =	y
Triangular trough, = 90°, bisector vertical, depth = y, slant depth = d	$\frac{d}{4} = \frac{y}{2\sqrt{2}}$
Trapezoid (depth = y, bottom width = b): Side slope 60° from horizontal	$\frac{yb + y/\sqrt{3}}{b + 4y/\sqrt{3}}$
Slide slope 45°	$\frac{y^2 + y^2}{b + 2\sqrt{2}y}$
* Values of K. If $S = (a - b)/(a + b)$,	
S = 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0	
K = 1.010 1.023 1.040 1.064 1.092 1.127 1.168 1.216 1.273	

11.3 FIELD SAMPLING

Collection of suspended solids in the field can be performed manually or automatically, however significant differences in results can be expected when sampling non-homogeneous systems such as raw municipal wastewaters as shown in Table 11.3.(4) In addition, automatic samplers with high intake velocities, of 2-10 ft/sec. will capture about one and a half to two times more solids than manual flow proportional or manual grab sampling methods. However, as the system becomes more homogeneous with respect to solids, intake velocities or sampling method becomes less important in obtaining comparable results as indicated by the final effluent values in Table 11.3.

Intake velocities above or below stream velocities for suspended sediment solids (specific gravity 2.65) within Stokes' Law, for example, Reynolds' number less than 1.0, do not result in any significant error as shown in Figure 11.2.(5) However, as the particle size increases, significant error occurs when the intake/stream velocity ratio varies from 1.0. This relationship (Figure 11.3) between the Relative Sampling Rate Ratio as error in concentration has a negative slope. When the intake velocity is less than the stream velocity, more solids will be collected and when the intake velocity exceeds the stream velocity, less solids shall be collected.

The rationale for this inverse relationship is illustrated in Figure 11.4. Therefore, in order to insure representative sampling, the intake/stream velocity ratio should be unity (isokinetic flow).

TABLE 11.3 RICHARDS-GEBAUR SEWAGE TREATMENT PLANT NON-FILTERED SOLIDS COMPARISON RATIO OF SAMPLING METHOD VALUE TO MANUAL FLOW VALUE

Station	Sample Method	Date			Average	Intake Velocity ft/sec.
		May 21	May 22	May 23		
Influent	QCEC	2.099	1.155	1.755	1.669	2-5
	ISCO	0.991	0.431	1.046	0.942	2
	Manual Flow	1.0	1.0	2.0	1.0	--
	Manual Grab	1.223	0.697	0.820	0.907	--
Primary Effluent	Hants	3.141	1.537	1.449	2.042	2.5
	Sigmamotor	0.783	0.700	0.968	0.817	0.25
	Manual Flow	1.0	1.0	1.0	1.0	--
	Manual Grab	0.981	0.975	1.170	1.042	--
Final Effluent	Hants	1.354	0.743	1.387	1.161	2.5
	Brailsford	0.822	0.769	1.225	0.939	.02
	Manual Flow	1.0	1.0	1.0	1.0	--
	Manual Grab	0.951	0.794	1.209	0.985	--

11.4 LABORATORY SUBSAMPLING

Subsampling from previously collected field samples may be subject to error resulting from segregation effects, such as particle size and specific gravity. As shown in Figure 11.5, the shake and pour technique achieves 93% recovery of solids with specific gravities in the range of 2.2-2.6 and particle sizes less than 50 microns; magnetic stirring improves percent recoveries.

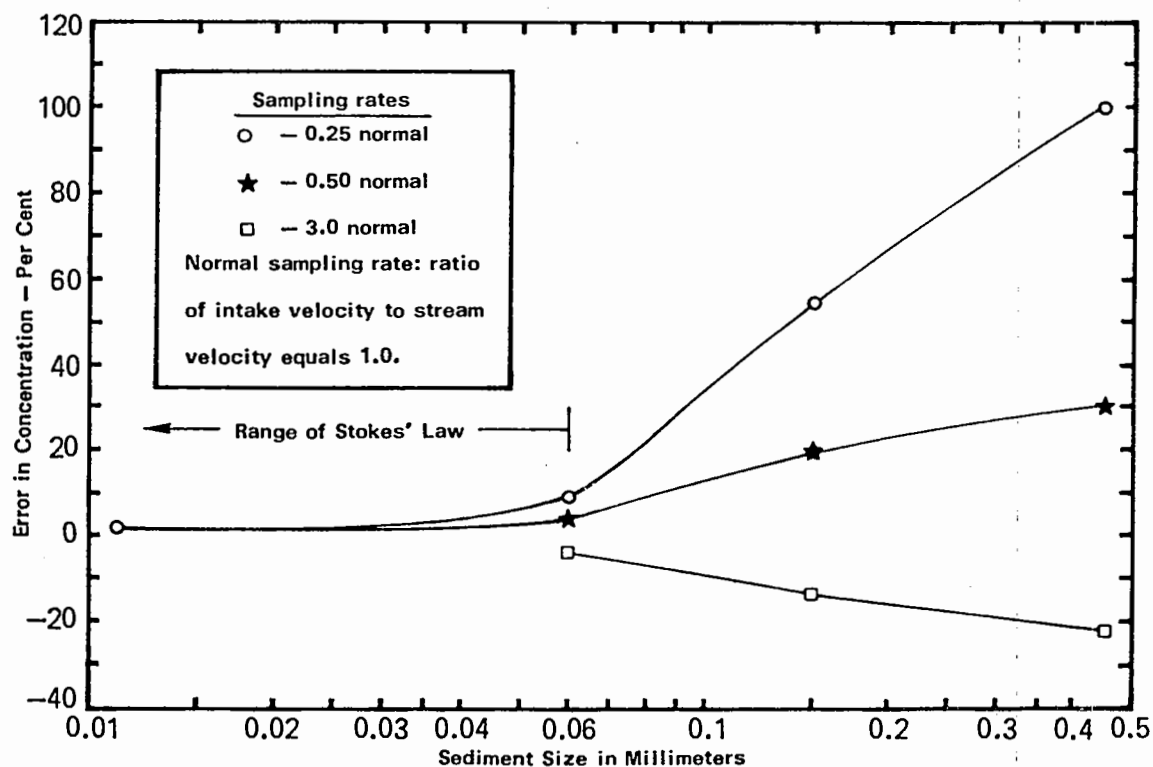


Figure 11.2 Relation of sediment size to errors in sediment concentration.

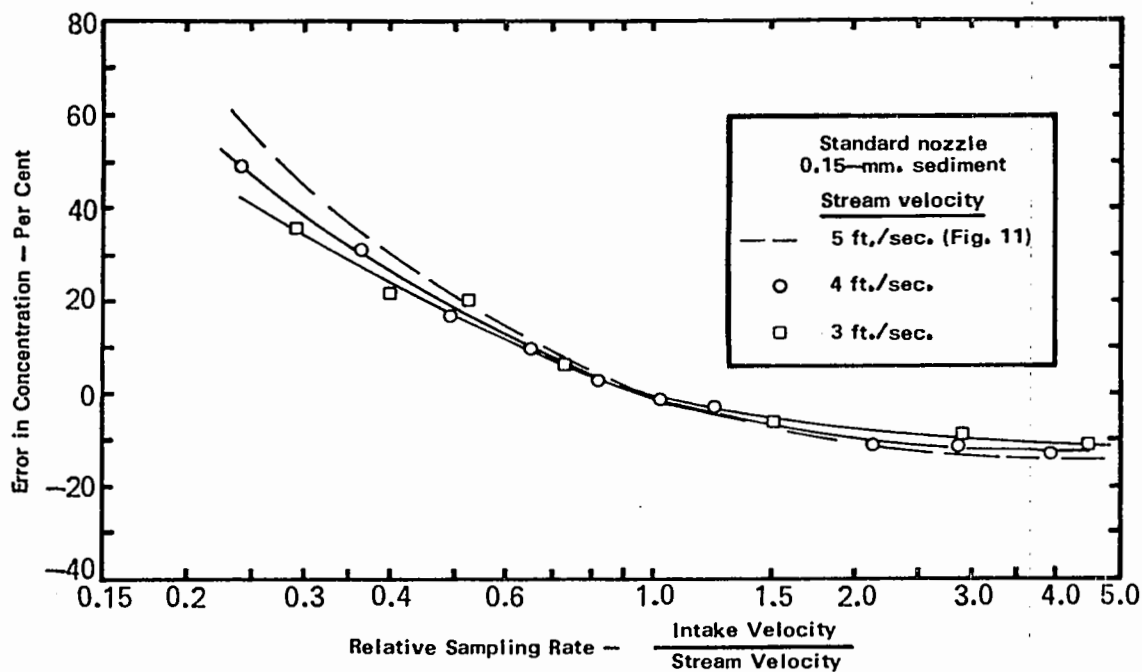
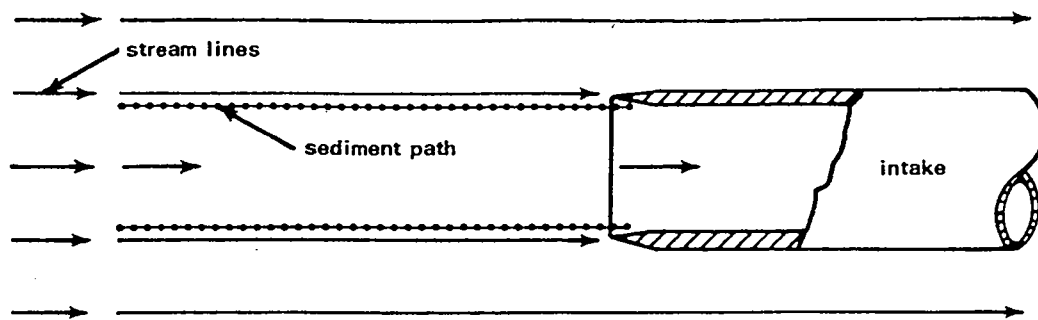
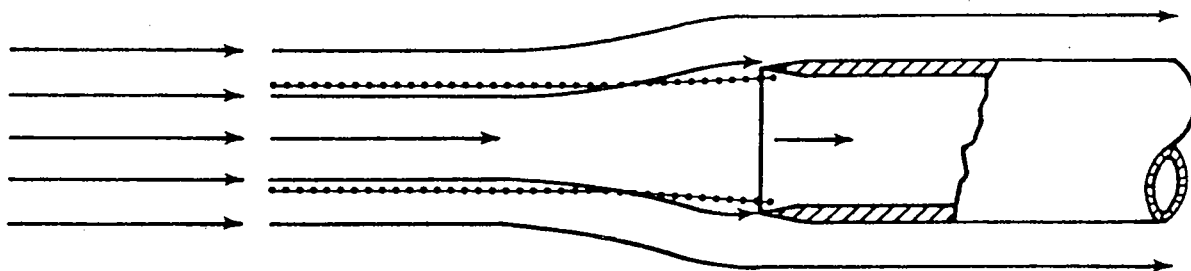


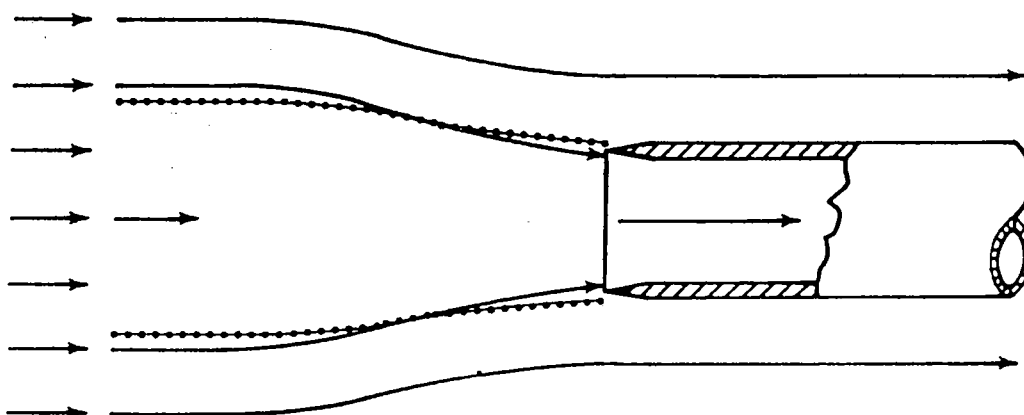
Figure 11.3 Effect of stream velocity on errors in sediment concentration.



a. Normal sampling rate — intake velocity equal to stream velocity.



b. Sampling rate below normal — as illustrated, ratio of intake velocity to stream velocity approximately $1/3$.



c. Sampling rate above normal — as illustrated, ratio of intake velocity approximately 3.

Figure 11. 4 Flow patterns at mouth of sampler intake.

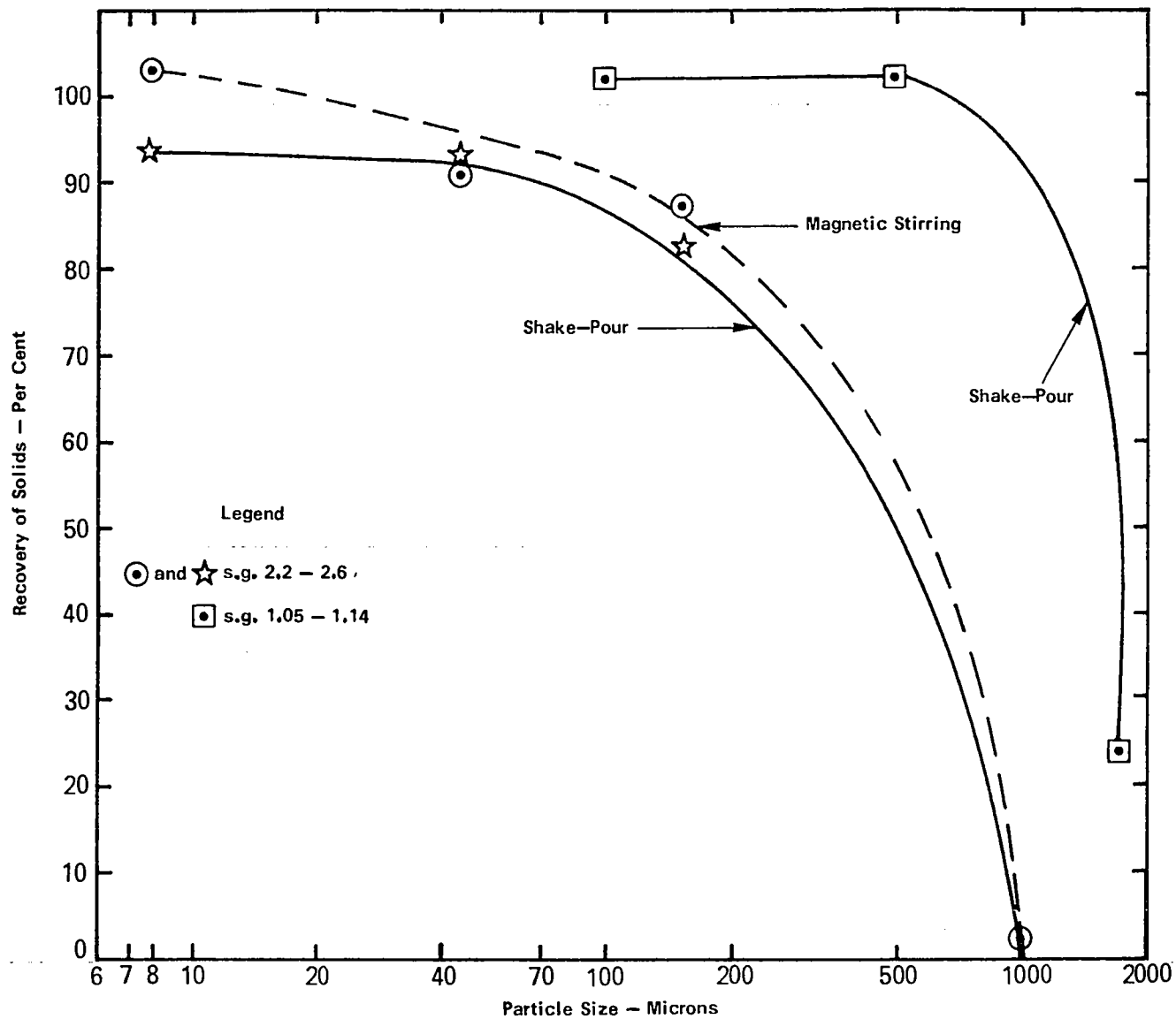


Figure 11.5 Percent recovery vs particle size during subsampling with different mixing techniques

Subsampling recoveries of 100% for solids having specific gravities ranging from 1.05-1.14 can be expected up to 500 microns. Therefore, to insure representative subsampling, the entire sample should be thoroughly blended and as large an aliquot used as possible.

11.5 GUIDELINES FOR SAMPLING OF SUSPENDED SOLIDS

Minimize sampling errors caused by segregation effects by sampling in a well mixed or turbulent zone.

Minimize random sampling errors in the laboratory by homogenizing the sample and using as large a sample aliquot as possible.

Maintain the flow rate in the sample lines to effectively transport suspended solids. For horizontal runs, the velocity must exceed the scouring velocity and in vertical runs, the velocity must exceed the settling velocity of the particle.

For solids falling within the range of Stokes' Law, consistent representative samples can be obtained at intake/stream ratio either greater or less than 1.0. For solids falling outside Stokes' Law, an intake/stream ratio of 1.0 is recommended.

The geometry of the intake has little effect upon the representativeness of the sample, however, the intake should face into the stream at no more than 20 degrees from the direction of stream flow.

11.6 REFERENCES

1. Physical and Settling Characteristics of Particulates in Storm and Sanitary Wastewaters. EPA 670/2-75-011, April, 1975.
2. Design and Testing of a Prototype Automatic Sewer Sampling System. EPA 600/2-76-006, March, 1976.
3. WPCF Manual of Practice. No. 9, ASCE, 1970. p. 88.
4. Harris, D.J., W.J. Keffer. Wastewater Sampling Methodologies and Flow Measurement Techniques. EPA 907/9-74-005, 1974.
5. Interagency Committee on Water Resources, A Study of Methods Used in the Measurement of Analysis of Sediment Loads in Streams: Laboratory Investigation of Suspended Sediment Samplers, Report No. 5, 1940.

CHAPTER 12

SAMPLING, PRESERVATION AND STORAGE CONSIDERATIONS

FOR TRACE ORGANIC MATERIALS

Organic compounds in water and wastewater are regulated by the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA).

The SDWA has established maximum contaminant levels (1)(2) for the following organic chemicals:

- | | | |
|----|---------------------------|----------------------|
| a) | Chlorinated hydrocarbons: | |
| | Endrin | Methoxychlor |
| | Lindane | Toxaphene |
| b) | Chlorophenoxy: | |
| | 2,4-D | 2,4,5-TP (Silvex) |
| c) | Trihalomethanes: | |
| | Trichloromethane | Bromodichloromethane |
| | Dibromochloromethane | Tribromomethane |

Listed in Table 12.1 are chemicals which have been detected in drinking water supplies and for which the possibility of adverse health effects exists. The presence of these chemicals is indicative of chemical pollution; this list is not exhaustive, but serves merely as a guide.(3)

A court settlement agreement involving the Natural Resources Defense Council, et al. and the U.S. Environmental Protection Agency (EPA Consent Decree) resulted in EPA publishing a list of 65 compounds and classes of compounds (Table 12.2). The Consent Decree required that EPA regulate these compounds via the Federal Water Pollution Control Act (subsequently amended by the Clean Water Act). EPA's expanded list of organic priority pollutants (Table 12.3) is an outgrowth of the Consent Decree's list of 65.

Specific toxic pollutant effluent standards will be promulgated for the organic priority pollutants, thus far they have been promulgated (4)(5)(6) for the following:

Aldrin/Dieldrin	Endrin
Benzidine	Toxaphene
DDT (DDD, DDE)	PCB's

TABLE 12.1 CHEMICAL INDICATORS OF INDUSTRIAL CONTAMINATION (23)

I. Aliphatic halogenated hydrocarbons:

Methane derivatives:	
Dichloromethane	Dichlorodifluoromethane
Trichlorofluoromethane	Carbon Tetrachloride
Ethane derivatives:	
1,1-dichloroethane	1,1,1-trichloroethane
1,2-dichloroethane	1,1,2-trichloroethane
hexachloroethane	1,1,2,2-tetrachloroethane
Unsaturated hydrocarbons:	
Trichloroethylene	1,2-dichloroethene
tetrachloroethylene	1,3-dichloropropene
Vinyl chloride	Hexachlorobutadiene
1,1-dichloroethene	2-chlorovinyl ether
Other halogenated compounds:	
1,1-dichloropropane	Bis(2-chloroethyl) ether
bis(2-chloroisopropyl) ether	

II. Cyclic aliphatic compounds:

Chlorinated hydrocarbons:	
Lindane	Kepone
BHC	Toxaphene
Cyclodienes:	
Chlordane	Heptachlor
Aldrin	Heptachlor epoxide
Dieldrin	Endrin
Hexachlorocyclopentadiene	

III. Aromatic hydrocarbons:

3,4-benzofluoranthene	fluoranthene
benzo(k)fluoranthene	indeno(1,2,3,c,d)pyrene
1,12-benzoperylene	benzo(a)pyrene
Benzenes:	
Benzene	Ethylbenzene
Toluene	Propylbenzene
Xylenes	Styrene
Halogenated aromatics:	
Chlorinated naphthalenes	DDE
Chlorobenzene	DDD

TABLE 12.1 (continued)

Halogenated aromatics:(continued)	
Dichlorobenzenes	Chlorophenols
Polychlorinated biphenyls	Trichlorobenzenes
Pentachlorophenol	4-bromophenylphenyl ether
Bromobenzene	4-chlorophenylphenyl ether
DDT	Hexachlorobenzene
Other aromatic hydrocarbons:	
Nitrobenzene	Phthalate esters
Dinitrotoluene	Atrazine

TABLE 12.2 65 TOXIC POLLUTANTS OR CLASSES OF TOXIC POLLUTANTS (21)

Acenaphthene	Ethylbenzene
Acrolein	Fluoranthene
Acrylonitrile	Haloethers
Aldrin/Dieldrin	Halomethanes
Antimony and compounds	Heptachlor and metabolites
Arsenic and compounds	Hexachlorobutadiene
Asbestos	Hexachlorocyclohexane (all isomers)
Benzene	Hexachlorocyclopentadiene
Benzidine	Isophorone
Beryllium and compounds	Lead and compounds
Cadmium and compounds	Mercury and compounds
Carbon tetrachloride	Naphthalene
Chlordane (technical mixture and metabolites)	Nickel and compounds
Chlorinated benzenes (other than dichlorobenzenes)	Nitrobenzene
Chlorinated ethanes (including 1,2 dichloroethane 1,1,1-trichloroethane, and hexachloroethane)	Nitrophenols (including 2,4-dinitrophenol, dinitrocresol)
Chloroalkyl ethers (chloromethyl, chloroethyl, and mixed ethers)	Nitrosamines
Chlorinated naphthalene	Pentachlorophenol
Chlorinated phenols	Phenol
Chloroform	Phthalate esters
2-chlorophenol	Polychlorinated biphenyls (PCB's)
Chromium and compounds	Polynuclear aromatic hydrocarbons (including benzanthracenes, benzopyrenes, benzo[a]fluoran- thene, chrysenes, dibenzanthracenes and indeno[1,2,3-cd]pyrenes)
Copper and compounds	Selenium and compounds
Cyanides	Silver and compounds
DDT and metabolites	2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)
Dichlorobenzenes (1,2-, 1,3- and 1,4-dichlorobenzenes)	Tetrachloroethylene
Dichlorobenzidine	Thallium and compounds
Dichloroethylenes (1,1- and 1,2-dichloroethylenes)	Toluene
2,4-dichlorophenol	Toxaphene
Dichloropropane and dichloropropene	Trichloroethylene
2,4 Dimethylphenol	Vinyl Chloride
Dinitrotoluene	Zinc and compounds
Diphenylhydrazine	
Endosulfan and metabolites	
Endrin and metabolites	

TABLE 12.3 PRIORITY POLLUTANTS

I. Phthalate esters:

Dimethyl phthalate	Di-n-octyl phthalate
Diethyl phthalate	Bis(2-ethylhexyl)phthalate
Di-n-butyl phthalate	Butylbenzyl phthalate

II. Haloethers

Bis(2-chloroethyl)ether	Bis(2-chloroethoxy)methane
Bis(2-chloroisopropyl)ether	4-chlorophenylphenyl ether
2-chloroethylvinyl ether	4-bromophenylphenyl ether

III. Chlorinated hydrocarbons:

Hexachloroethane	1,3-dichlorobenzene
Hexachlorobutadiene	1,4-dichlorobenzene
Hexachlorocyclopentadiene	1,2,4-trichlorobenzene
1,2-dichlorobenzene	Hexachlorobenzene
2-chloronaphthalene	

IV. Nitroaromatics and Isophorone:

Nitrobenzene	2,4-dinitrotoluene
2,6-dinitrotoluene	Isophorone

V. Nitrosoamines:

N-nitrosodimethylamine	N-nitrosodipropylamine
N-nitrosodiphenylamine	

VI. Dioxin:

2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)

VII. Benzidines:

Benzidine	3,3-dichlorobenzidine
-----------	-----------------------

VIII. Phenols:

Phenol	Pentachlorophenol
2,4-dimethylphenol	4-chloro-3-methylphenol
2-chlorophenol	2-nitrophenol
2,4-dichlorophenol	4-nitrophenol
2,4,6-trichlorophenol	2,4-dinitrophenol
4,6-dinitro-2-methylphenol	

TABLE 12.3 (continued)

IX. Polynuclear aromatics:

Acenaphthene	Acenaphthylene
Fluoranthene	Anthracene
Naphthalene	Benzo(g,h,i)perylene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Phenanthrene
Benzo(b)fluoranthene	Dibenzo(a,h)anthracene
Benzo(k)fluoranthene	Indeno(1,2,3-cd)pyrene
Chrysene	Pyrene

X. Pesticides & PCB's:

Aldrin	Heptachlor epoxide
Dieldrin	Alpha-BHC
Chlordane	Beta-BHC
DDD	Delta-BHC
DDE	Gamma-BHC
DDT	Toxaphene
A-endosulfan	Aroclor 1242
B-endosulfan	Aroclor 1254
Endosulfan	Aroclor 1221
Endrin	Aroclor 1232
Endrin aldehyde	Aroclor 1248
Heptachlor	Aroclor 1260
Toxaphene	Aroclor 1016

XI. Purgeables:

Benzene	Chloroform
Chlorobenzene	1,1-dichloroethylene
Toluene	1,2-transdichloroethylene
Ethylbenzene	1,2-dichloropropane
Carbon tetrachloride	1,1-dichloropropylene
1,2-dichloroethane	Methylchloride
1,1,1-trichloroethane	Methylenechloride
1,1-dichloroethane	Methylbromide
1,1,2-trichloroethane	Bromoform
1,1,2,2-tetrachloroethane	Dichlorobromomethane
Chloroethane	Trichloroethylene
Chlorodibromomethane	Vinyl chloride
Tetrachloroethylene	

XII. Acrolein & Acrylonitrile:

Acrolein	Acrylonitrile
----------	---------------

Analytical procedures for the identification of organic compounds can be found in a number of publications.(7 - 22) However, analytical results are only meaningful if the sample analyzed is truly a representative sample of the media you are testing. Chemical analysis for organics present at trace levels places high demands on sampling techniques.

12.1 SAMPLE COLLECTION METHOD

The method of sampling can either be manual or automatic. Sampling practices, as specified in Chapter 2, should be followed, except as indicated in this chapter.

12.1.1 Manual Sampling

The considerations outlined in Chapter 2 are applicable. However, the sample collector and container should be constructed of borosilicate glass to minimize sample contamination. Grab samples obtained for analyses of purgeable organics are sealed to eliminate entrapped air.(7) This sample collected without headspace, is illustrated in Figure 12.1.

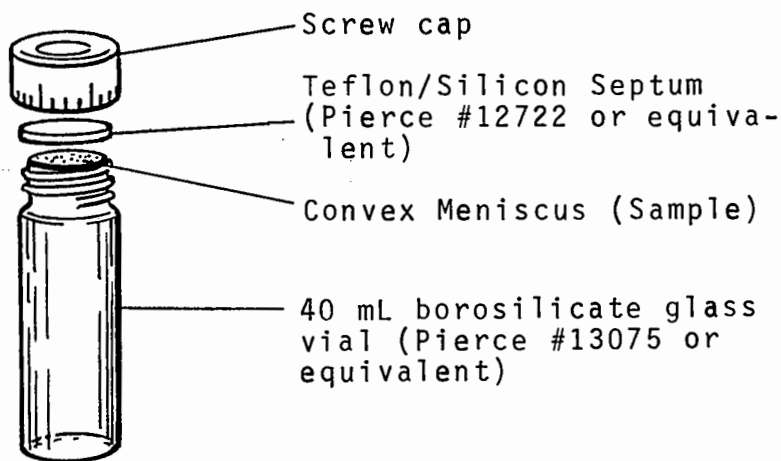


Figure 12.1 Collection Bottle (21,22)

12.1.2 Automatic Sampling

Although continuous automatic sampling is probably the best method for collecting truly representative samples, certain precautions must be taken.

Automatic sampling equipment must be free of Tygon and other potential sources of contamination such as plastic, or rubber components.(23) Tygon tubing is a potential source of phthalate ester contamination. Teflon is acceptable and may be used in the sampling system as required.

Automatic samplers used to obtain samples for trace organics analyses may need special design features. An experimental sampler has been developed which is capable of collecting grab samples for purgeable organics analysis and collecting samples on accumulator columns (adsorption/absorption columns) for non-purgeable organics analyses.(24) All system components in contact with the sample are either constructed of Teflon or glass; this includes a specially designed Teflon-bellows pump. Illustrations of this system are shown in Figures 12.2 through 12.6.

Sampling systems utilizing carbon or macroreticular resin in columns have been employed for sampling organics in ground water.(25 - 27) The accumulator column in these systems is located between the water to be sampled and the pump, therefore, special Teflon type pumps are not needed. These type systems are illustrated in Figures 12.7 through 12.10.

Automatic samplers can be used to collect composited samples. EPA's 600 series methods for analyzing non-volatile organic priority pollutants reference these types of automatic samplers.

12.2 SEDIMENT SAMPLING

Sediment sampling can be classified into two general categories:

1. suspended sediments
2. bottom sediments

12.2.1 Suspended Sediment Samplers

Suspended sediment samplers should be in accordance with the suspended solids sampling considerations of Chapter 11. When employing any suspended sediment sampler for the collection of samples to be analyzed for organics, materials such as Neoprene and Tygon must be replaced by inert materials such as Teflon. In addition, valves must be cleaned to remove oil.

12.2.2 Bottom Sediment Samplers

Bottom sediment samplers are designed to obtain a sample of the sediment mixture of which the stream bed is composed. This should be differentiated from the bed-load. Refer to Chapter 8, Tables 8.4 and 8.5 for a listing of these types of samplers. Replacement of contaminating materials, such as Tygon or Neoprene, with inert materials should be considered. When replacement of contaminating materials is not possible or not practical, it may be necessary to obtain specially constructed sediment collectors.

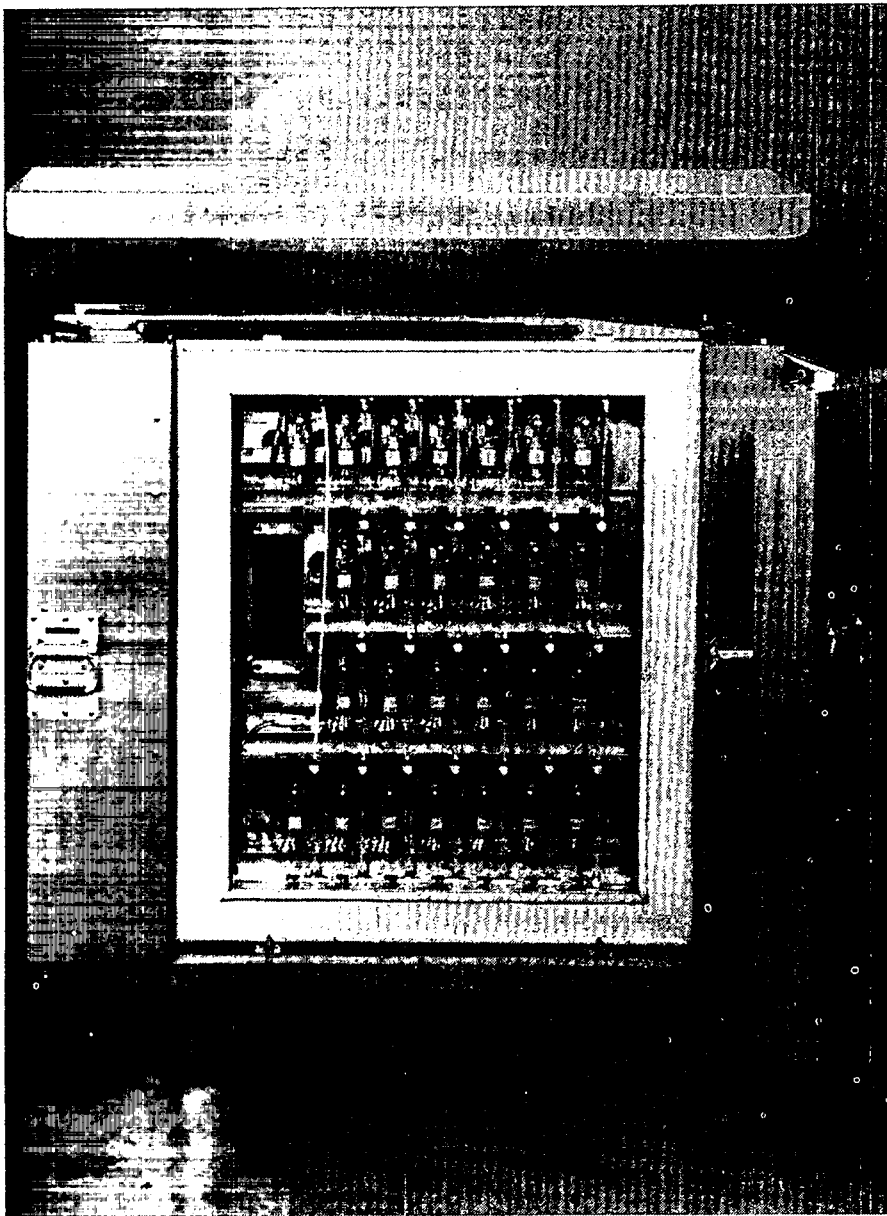


Figure 12.2 Automatic sampler opened to show the 26 purgeable sample bottles in position.

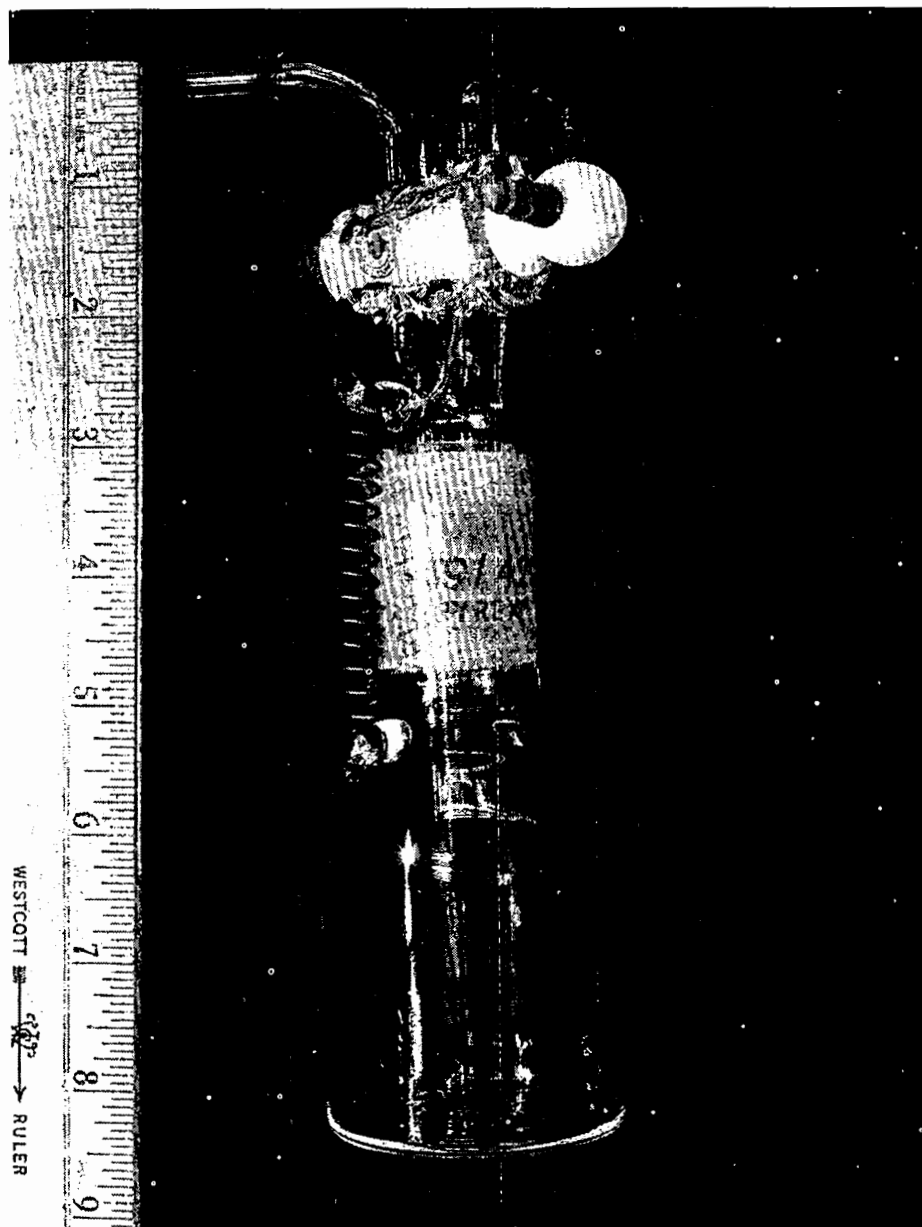


Figure 12.3 A 140 mL purgeable sample bottle for the automatic sampler.

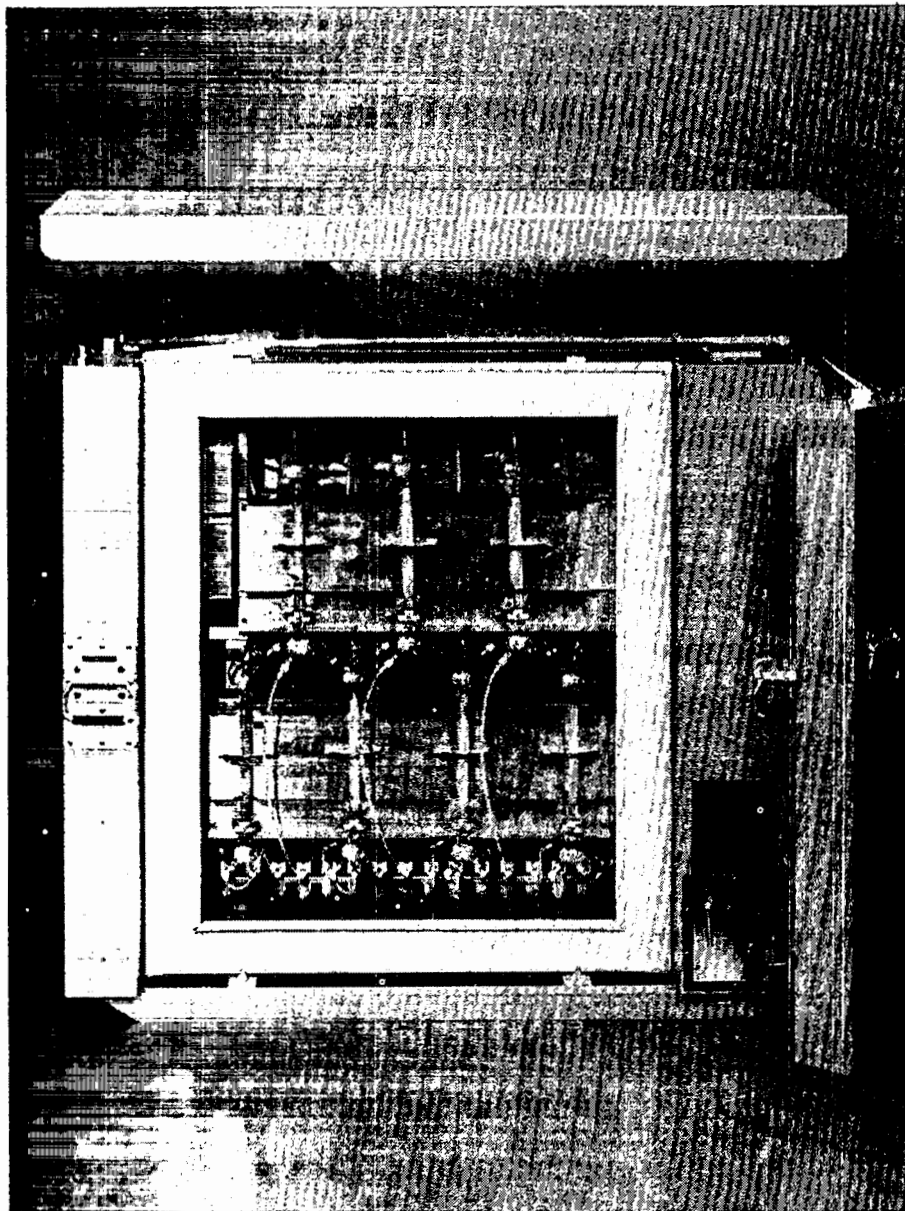


Figure 12.4 Automatic sampler opened to show 7 or the 14 accumulator columns. Another bank of 7 is located behind the visible bank.

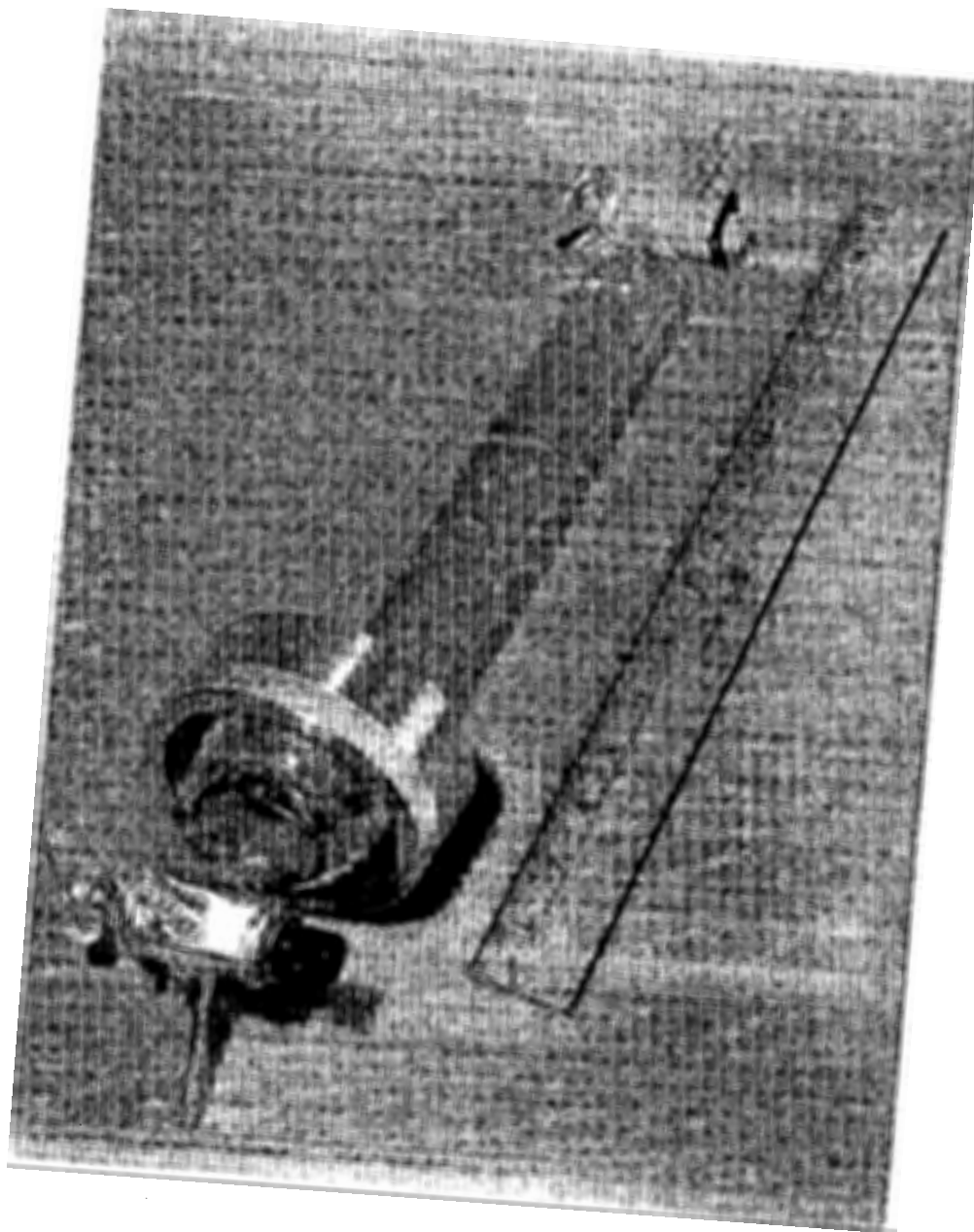


Figure 12.5 A 1.8 x 27 cm empty accumulator column for the automatic sampler.

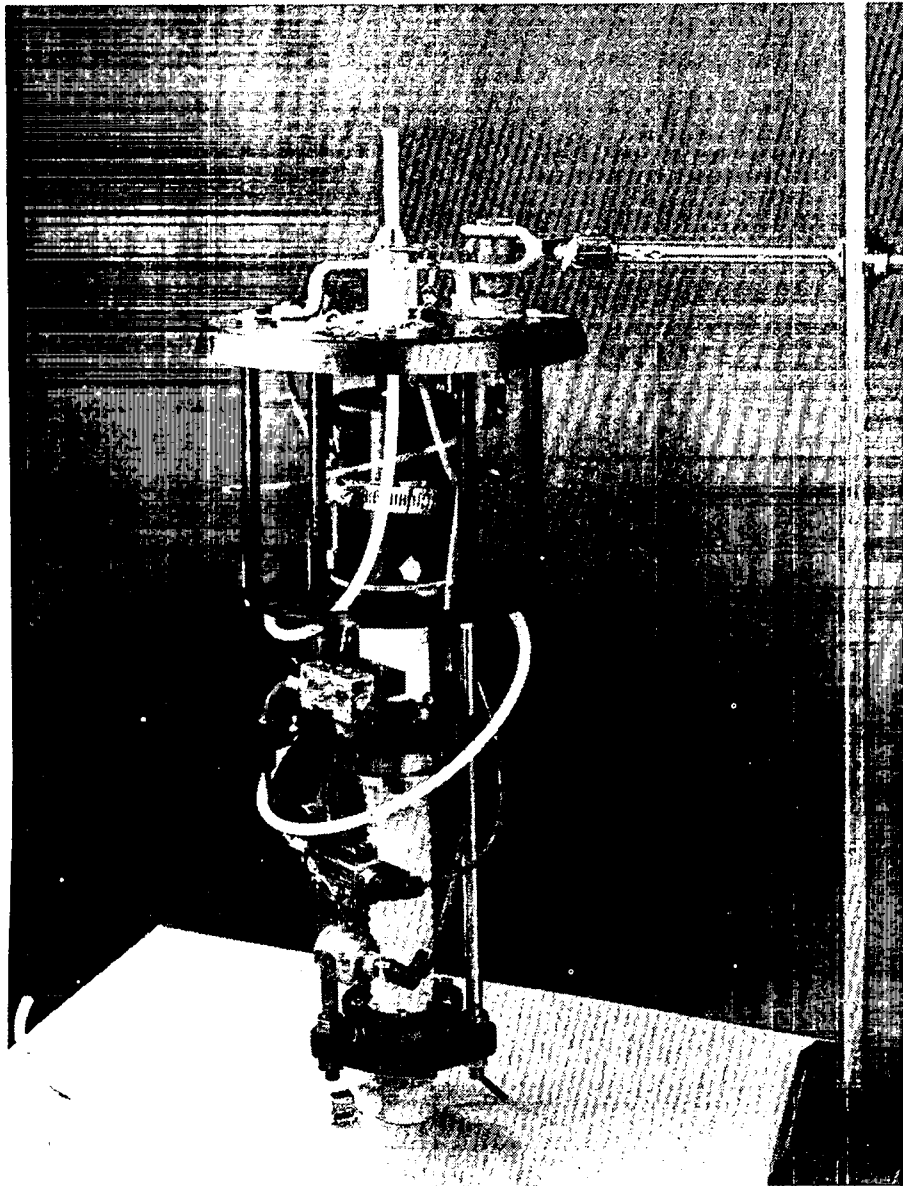
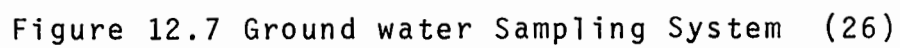


Figure 12.6 Automatic sampler pump with container removed.
Teflon bellows are at the bottom.



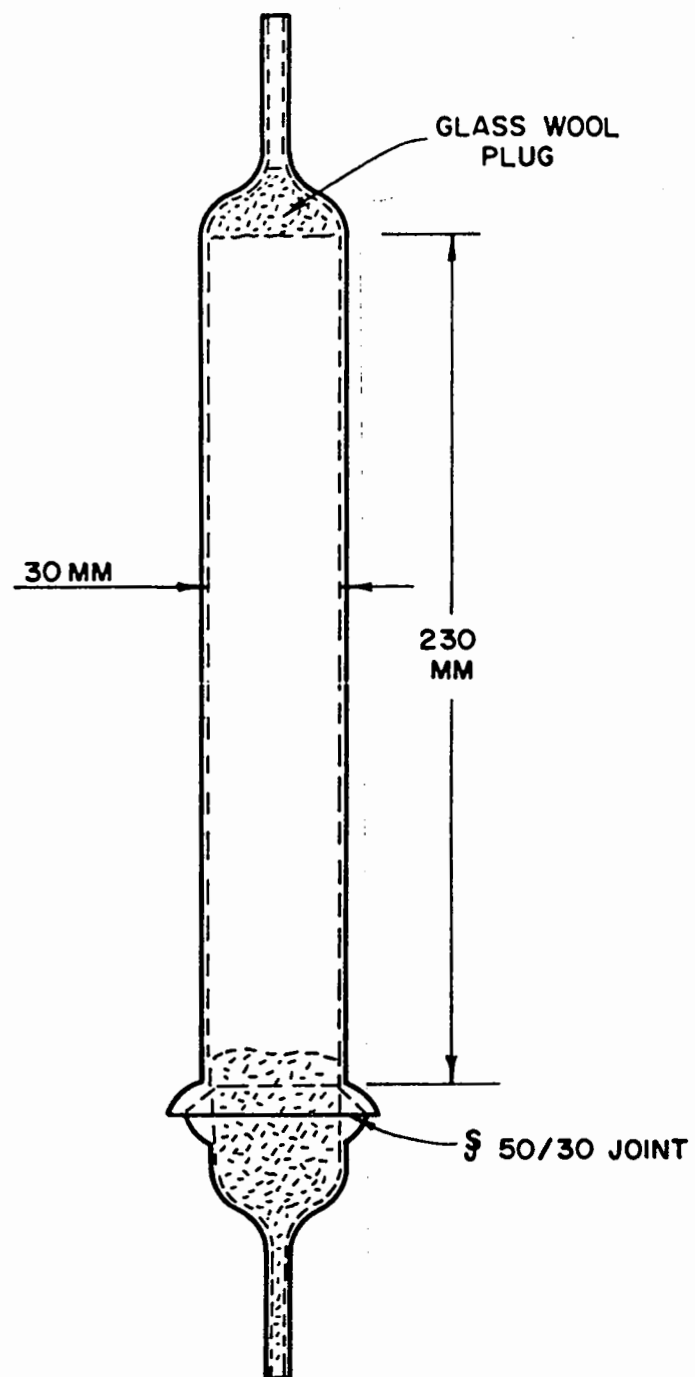


Figure 12.8 Carbon adsorption column (27)

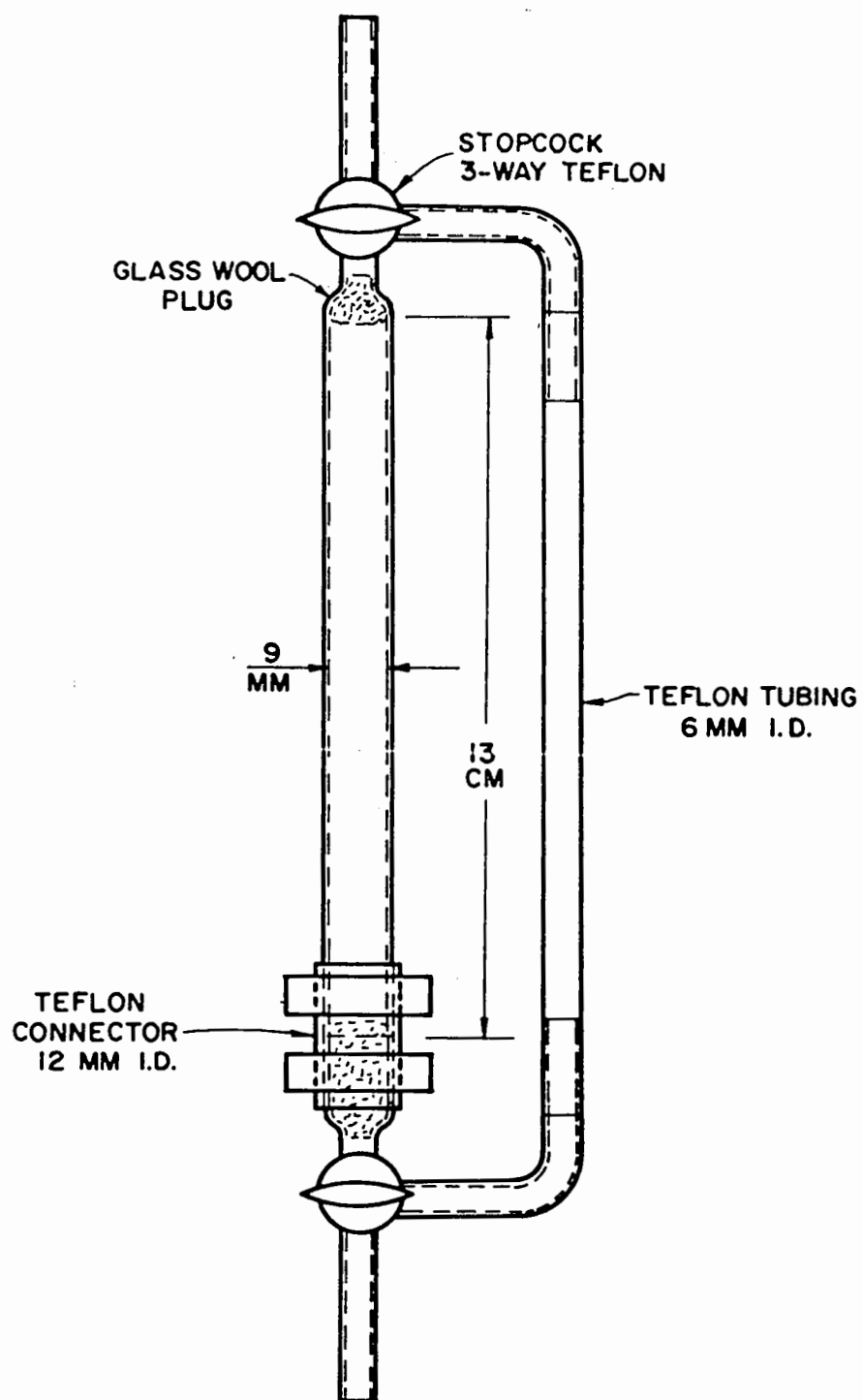


Figure 12.9 Resin adsorption column (27)

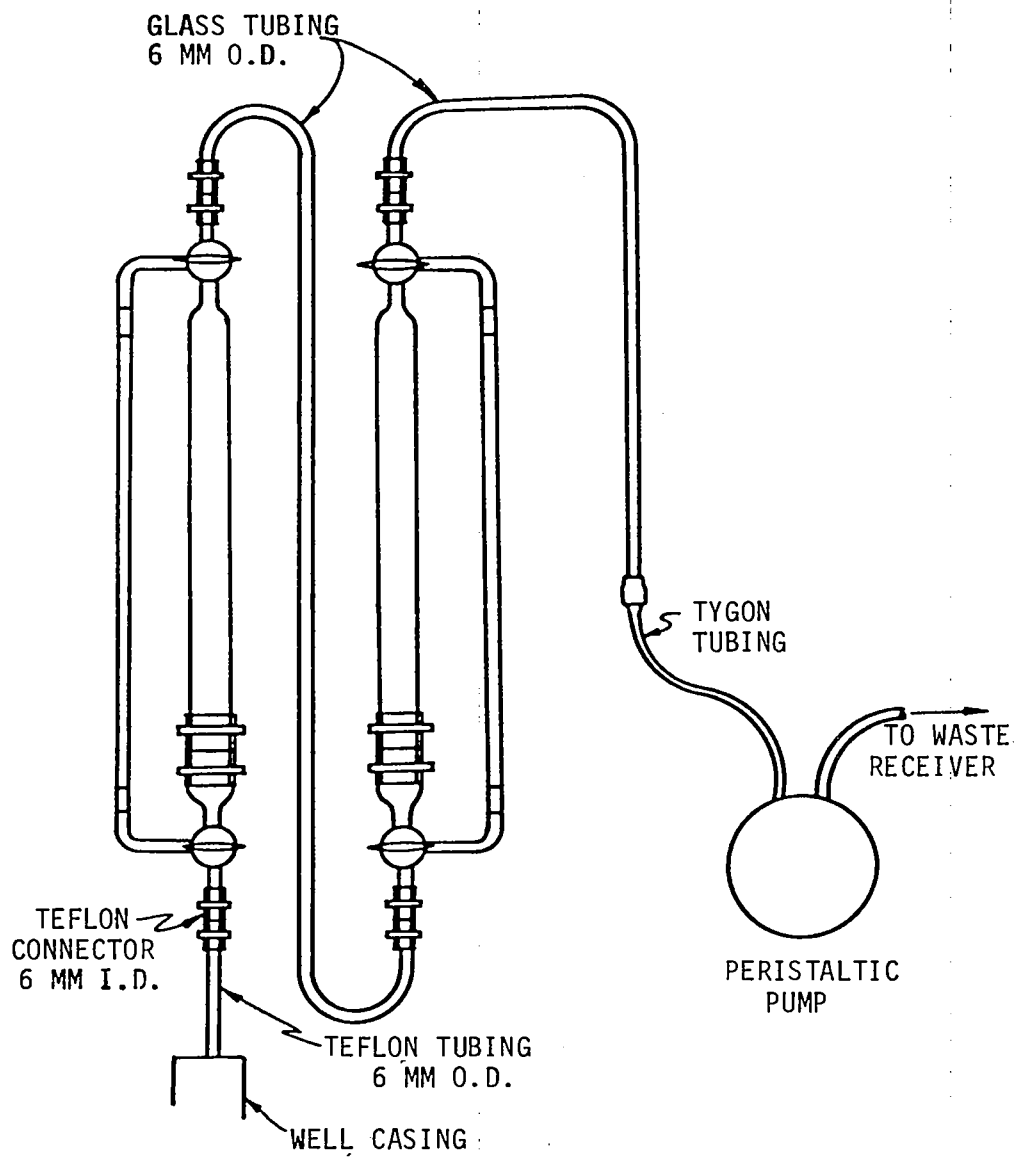


Figure 12.10 Ground-water sampling system (27)

12.2.2.1 Sampling Site (28)

The selection of sampling sites when collecting bottom sediments for organic analyses is extremely important. Bottom sediments, within any river, stream, or other body of water tend to be heterogeneous. Some bottom areas are primarily sand, while others are primarily silt and clay. Organic pollutants adsorbed on sediments that possess a large surface-to-volume ratio, therefore, finer sediments such as silts and clays will exhibit higher concentrations of organics, than will coarser sediments such as sands and gravels. Sample sites should be selected at depositing areas where silt and clay settle out due to low current speeds. Examples are: inside of river bends, downstream of islands or other obstructions, and near the center of water mass in ponds, lakes, and reservoirs.

Do not sample areas that are exposed during low flow or low tide conditions or at points immediately following the confluence of two streams.

Collect representative samples using random sampling techniques and the grid systems specified in Chapter 8. Particle sizes should not exceed 2 mm.

12.2.2.2 Sampling Equipment (28)

Sampling equipment should be designed to minimize disturbance of the top layers of sediments and minimize the loss of low density deposits during the sampling process. Drag buckets and scoops are not recommended for trace organic sampling. All samplers, regardless of type, disturb sediment fines, however, if precautions are taken, the disturbance can be minimized. Recommended sampling equipment and their limitations are summarized in Table 12.4.

12.3 SAMPLING LOCATION

The factors which influence the sampling location should be taken into account as indicated in Chapter 2.

12.4 SAMPLE CONTAINER

The configuration and materials of a container which can be utilized in the collection and storage of organic containing samples are somewhat varied. However, the following criteria should be met:

1. Non-purgeable samples must be collected in amber glass containers in a liter or quart volume and preferably of French or Boston round design.(22)(23) Various glass vials have also proved to be adequate.(22)(27)(29)(30)

**TABLE 12.4 SUMMARY OF BOTTOM SAMPLING EQUIPMENT
(DEVICES LISTED IN DESCENDING ORDER OF RECOMMENDATION) (28)**

Device	Use	Advantages	Disadvantages
Teflon or Glass Tube	Shallow wadeable waters or deep waters if SCUBA available. Soil or semi-consolidated deposits	Preserves layering and permits historical study of sediment deposition. RAPID - samples immediately ready for laboratory shipment. Minimal risk of contamination. Inexpensive.	Small sample size requires repetitive sampling.
Hand Cover with removable Teflon or glass liners.	Same as above except more consolidated sediments can be obtained. Use extended to waters of 4-6 feet by the use of extension rods.	Handles provide for greater ease of substrate penetration.	Requires removal of liners before repetitive sampling. Slight risk of metal contamination from barrel and core cutter.
Eckman or Box-Dredge, line or pole operated.	Soft to semi-soft sediments. Can be used from boat, bridge, or pier in waters of various depths.	Obtains a larger sample with respect to coring tubes. Can be subsampled through box-lid. Pole operated sampler provides greater control and minimizes disturbance of the "fines".	Possible incomplete jaw closure and sample loss. Possible shock wave which may disturb the fines. Metal construction may introduce contaminants.
Gravity corers i.e. Phleger Corer	Deep lakes and rivers. Semi-consolidated sediments	Low risk of sample contamination.	Small sample, requires repetitive operation and removal of liners. Time consuming.
Ponar Grab Sampler	Deep lakes, rivers, and estuaries. Useful on sand, silt, or clay.	Most universal grab sampler. Adequate on most substrates. Large sample obtained intact, permitting subsampling.	Shock wave from descent may disturb "fines". Possible incomplete closure of jaws and sample loss. Possible contamination from metal frame construction. Sample must be further prepared for analysis.
BHI-53 Piston Corer	Waters of 4-6 feet deep when used with extension rod. Soft to semi-consolidated deposits.	Piston provides for greater sample retention.	Cores must be extruded on site to other containers - metal barrel introduces risk of metal contamination.
USDM 60	Sampling moving waters from a fixed platform.	Streamlined configuration allows sampling where other devices could not achieve proper orientation.	Possible contamination from metal construction. Subsampling difficult. Not effective for sampling fine sediments.
Petersen Grab Sampler	Deep lakes, rivers, and estuaries. Useful on most substrates	Large sample; can penetrate most substrates.	Heavy, may require winch. No cover lid to permit subsampling. All other disadvantages of Eckman and Ponar.
Orange Peel Grab Smith McIntyre Grab	Deep lakes, rivers, and estuaries. Useful on most substrates.		
Scoops, drag buckets	Various environmental degrading.		

2. Container caps should be threaded to screw onto the container. Caps must be lined with Teflon.(22)(23) Foil may be substituted if sample is not corrosive.(22)
3. Purgeable sample must be collected in 40 mL borosilicate glass vials with screw caps (Pierce #13075 or equivalent). The septa used must be Teflon faced silicon (Pierce #12722 or equivalent). (22)

12.5 SAMPLING PROCEDURE AND PRETREATMENT OF SAMPLE EQUIPMENT

12.5.1 Pretreatment of Equipment

The pretreatment technique should be dictated by the analysis to be performed. The general pretreatment technique for sample and storage containers is to:

1. Wash bottles with hot detergent water.
2. Rinse thoroughly with tap water followed by three or more rinses with organic-free water.
3. Rinse with interference free redistilled solvent such as acetone or methylene chloride and dry in contaminant free air at room temperature. Protect from atmospheric or other sources of contamination. Caps and liners for bottles must also be solvent rinsed as above.

If automatic samplers are to be employed, use the peristaltic pump type with a single 8 - 10 liter (2.5 - 3.0 gallons) glass container. Vacuum type automatic samplers can be used if sample containers are glass. The procedure outlined above should be followed for the pretreatment of the containers. In addition all tubing and other parts of the sampling system must be scrubbed with hot detergent water and thoroughly rinsed with tap water and blank water prior to use. Further rinsing with interference free acetone or methylene chloride is advised when tubing and other parts permit, i.e., are not susceptible to dissolution by the solvent.

12.5.2 Sampling Procedure

Purgeables (22)(31)(32)

Collect grab samples in glass containers. The procedure for filling and sealing sample containers is as follows: Slowly fill each container to overflowing. Carefully set the container on a level surface. Place the septum Teflon side down on the convex sample meniscus. Seal the sample with the screw cap. To insure that the sample has been properly sealed, invert the sample and lightly tap the lid on a solid surface. The absence of entrapped air bubbles indicates a proper seal. If air bubbles are present, open the bottle, add additional sample, and reseal (in same manner as stated above). The sample must remain hermetically sealed until it is analyzed. Maintain samples at 4°C (39°F) during transport and storage prior to analysis. If the sample is

taken from a water tap, turn on the water and permit the system to flush. When the temperature of the water has stabilized, adjust the flow to about 500-mL/minute and collect samples as outlined above.

Non-Purgeables (22)(32)

Collect grab samples in glass containers. Conventional sampling practices should be followed, except that the bottle must not be pre-washed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of Tygon and other potential sources of contamination.

12.6 SAMPLE PRESERVATION AND STORAGE (32)

Analyze samples as soon as possible. Preserve and store samples collected for analyses via EPA's 600 Method Series as described below:

Method 601 - Purgeable Halocarbons

The samples must be iced or refrigerated at 4°C from the time of collection until extraction. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 mL will suffice for up to 5 ppm Cl₂) to the empty sample bottles just prior to shipping to the sampling site.

All samples must be analyzed within 14 days of collection.

Method 602 - Purgeable Aromatics

Collect about 500 mL sample in a clean container. Adjust the pH of the sample to about 2 by adding 1:1 diluted HCl while stirring vigorously. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 mL will suffice for up to 5 ppm Cl₂) to the empty sample bottles just prior to shipping to the sampling site.

The samples must be iced or refrigerated at 4°C from the time of collection until extraction.

All samples must be analyzed within 14 days of collection.

Method 603 - Acrolein and Acrylonitrile

The samples must be iced or refrigerated at 4°C from the time of collection until extraction. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl₂) to the empty sample bottles just prior to shipping to the sampling site.

If acrolein is to be analyzed, collect about 500 mL sample in a clean glass container. Adjust the pH of the sample to 4 to 5 using acid or base, measuring with narrow range pH paper. Samples for acrolein analyses receiving no pH adjustment must be analyzed within three days of sampling.

All samples must be analyzed within 14 days of collection.

Method 604 - Phenols

The samples must be iced or refrigerated at 4⁰ from the time of collection until extraction. At the sampling location fill the glass container with sample. Add 80 mg of sodium thiosulfate per liter of sample.

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 605 - Benzidines

The samples must be iced or refrigerated at 4⁰C from the time of collection to extraction. Benzidine and dichlorobenzidine are easily oxidized by materials such as free chlorine. For chlorinated wastes, immediately add 80 mg sodium thiosulfate per liter of sample.

If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4 ± 0.2 units to prevent rearrangement to benzidine. The sample pH should be adjusted to 2-7 with sodium hydroxide or sulfuric acid.

All samples must be extracted within seven days. Extracts may be held up to seven days before analysis if stored under an inert (oxidant free) atmosphere. The extract must be protected from light.

Method 606 - Phthalate Esters

The samples must be iced or refrigerated at 4⁰C from the time of collection until extraction.

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 607 - Nitrosamines

The samples must be iced or refrigerated at 4⁰C from the time of collection until extraction. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample. And, if diphenylnitrosamine is to be determined, adjust the pH of the water sample to pH 7 to 10 using sodium hydroxide or sulfuric acid. Record the volume of acid or base added.

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 608 - Organochlorine Pesticides and PCB's

The samples must be iced or refrigerated at 4°C from the time of collection until extraction. If the samples will not be extracted within 72 hours of collection, the sample should be adjusted to a pH range of 5.0 - 9.0 with sodium hydroxide or sulfuric acid. If aldrin is to be determined, and if residual chlorine is present, add sodium thiosulfate.

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 609 - Nitroaromatics and Isophorone

The samples must be iced or refrigerated at 4°C from the time of collection until extraction.

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 610 - Polynuclear Aromatic Hydrocarbons

The samples must be iced or refrigerated at 4°C from the time of collection until extraction. PAHs are known to be light sensitive, therefore, samples, extracts and standards should be stored in amber or foil wrapped bottles in order to minimize photolytic decomposition. Fill the sample bottle and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample.

All samples must be extracted within seven days, and analysis completely analyzed within 40 days of extraction.

Method 611 - Haloethers

The samples must be iced or refrigerated at 4°C from the time of collection until extraction. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of water.

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 612 - Chlorinated Hydrocarbons

The samples must be iced or refrigerated at 4°C from the time of collection until extraction.

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 613 - 2,3,7,8-Tetrachlorodibenzo-p-dioxin

The samples must be iced or refrigerated at 4°C from the time of collection until extraction. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of water. Protect the sample from light from the time of collection until analysis.

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

Method 624 - Purgeables (GC/MS)

The sample must be iced or refrigerated at 4°C from the time of collection until extraction. If the sample contains residual chlorine, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl₂) to the empty sample bottles just prior to shipping to the sample site, fill with sample just to overflowing, seal the bottle, and shake vigorously for one minute.

Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethylbenzene are susceptible to rapid biological degradation under certain environmental conditions.(3) Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. For this reason, a separate sample should be collected, acidified, and analyzed when these aromatics are to be determined. Collect about 500 mL of sample in a clean container. Adjust the pH of the sample to about 2 by adding HCl (1+1) while stirring. Check pH with narrow range (1.4 to 2.8) pH paper. Fill a sample container as described in Section 9.2. If chlorine residual is present, add sodium thiosulfate to another sample container and fill as in Section 9.2 and mix thoroughly.

All samples must be analyzed within 14 days of collection.

Method 625 - Base/Neutrals, Acids and Pesticides (GC/MS)

The samples must be iced or refrigerated at 4°C from the time of collection until extraction. The sample must be protected from light. If the sample contains residual chlorine, add 80 mg of sodium thiosulfate per liter of sample.

All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

12.7 REFERENCES

1. National Interim Primary Drinking Water Regulations, EPA-570/9-76-003.
2. Federal Register, Vol. 44, No. 231, November 29, 1979, pp. 68624-68707.
3. Federal Register, Vol. 43, No. 28, Table 1, February 9, 1978, p. 5780.
4. Federal Register, Vol. 41, June 10, 1976, p. 23576.
5. Federal Register, Vol. 41, June 30, 1976, p. 27012.
6. Federal Register, Vol. 41, July 23, 1976, p. 30468.
7. Bellar, T.A. and J.J. Lichtenberg. Determining Volatile Organics at Microgram-Per-Liter Level by Gas Chromatography. J. AWWA 66, pp 739-744, December, 1974.
8. Henderson, J.E., G.R. Peyton, and W.H. Glaze. Identification and Analysis of Organic Pollutants in Water. L.H. Keith, ed., pp. 105-111, Ann Arbor Science, Ann Arbor, Michigan, 1976.
9. Glaze, W.H., G.R. Peyton, O.D. Sparkman, and R.L. Stern. Proceedings of American Chemical Society, Southeast Southwest Regional Meeting. Paper #128, Memphis, Tennessee, October 29-31, 1975.
10. Duenbostel, B.F. Method of Obtaining GC/MS Data of Volatile Organics in Water Samples. Internal Report EPA, Region II Edison, New Jersey, May 14, 1973.
11. U.S. Environmental Protection Agency. Methods for Organic Water and Wastewaters. Cincinnati, Ohio, 1971.
12. Grob, K. Organic Substances in Porable Water and in Its Precursor: Part I Methods for Their Determination by Gas-Liquid Chromatography. Journal of Chromatography 84, p. 255, 1973.
13. Bertsch, W., E. Anderson, and G. Holzer. Trace Analysis of Organic Volatiles in Water by Gas Chromatography - Mass Spectrometry with Glass Capillary Columns. Journal of Chromatography 112, p. 701, 1975.
14. Sugar, J.W. and R.A. Conway. J. WPCF, 40 (9) 1922, September 1968.
15. American Society for Testing Materials. Annual Book of Standards. Part 23, Method D2908-70T, Philadelphia, Pennsylvania, 1973.
16. U.S. Environmental Protection Agency. Manual of Chemical Methods for Pesticides and Devices. July, 1976.
17. APHA, AWWA, WPCF, American Public Health Association. Standard Methods for the Examination of Water and Wastewater. 14th ed., Washington, DC, p. 1193, 1976.

18. Goerlitz, D.F. and E. Brown. Methods for Analysis of Organic Substances in Water. In: Techniques of Water-Resources Investigations. USGS, Book 5, Chapter A3, p.40, 1972.
19. Keith, L.H. Identification and Analysis of Organic Pollutants in Water. Ann Arbor Science, Ann Arbor, Michigan, p. 718, 1977.
20. American Society for Testing and Materials. Annual Book of Standards. Part 31, Philadelphia, Pennsylvania, 1977.
21. Budde, W.L. and J.W. Eichelberger. Development of Methods for Organic Analyses for Routine Application in Environmental Monitoring Laboratories. In: Identification and Analysis of Organic Pollutants in Water. L.H. Keith, ed. Ann Arbor Science Publishers, Ann Arbor, Michigan, 1976.
22. Federal Register, Vol. 44, No. 233. Guidelines Establishing Test Procedures for the Analysis of Pollutants; Proposed Regulations. Monday, December 3, 1979.
23. U.S. Environmental Protection Agency. Methods for Organic Compounds in Municipal and Industrial Wastewater. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, March, 1979.
24. Garrison, A.W., J.D. Pope, A.L. Alford and C.K. Doll. An Automatic Sampler, A Master Analytical Scheme and a Registry System for Organics in Water. In: Proceedings of the Ninth Annual Materials Research Symposium. National Bureau of Standards, Gaithersburg, MD. April, 1978 in press.
25. Dunlap, W.J., D.C. Shew, M.R. Scalf, R.L. Crosby and J.M. Robertson. Isolation and Identification of Organic Contaminants in Ground Water. In: Identification and Analysis of Organic Pollutants in Water, L.H. Keith, ed. pp. 453-478 Ann Arbor Science Publishers, Ann Arbor, Michigan, 1976.
26. Dunlap, W.J., J.F. McNabb, M.R. Scalf and R.L. Crosby, Sampling for Organic Chemicals and Microorganisms in the Subsurface. U.S. EPA 600/2-77-176, 1977.
27. Kopfler, F.C., R.G. Melton, R.D. Lingg, and W.E. Coleman. GC/MS Determination of Volatiles for the National Organics Reconnaissance Survey (NORS) of Drinking Water. In: Identification and Analysis of Organic Pollutants in Water. L.H. Keith, Ed. pp. 87-104 Ann Arbor Science Publishers, Ann Arbor, Michigan, 1976.
28. Freed, J.R., D.A. Abell, and R.E. Huddleston. Sampling Protocols for Analysis of Toxic Pollutants in Ambient Water, Bed Sediment, and Fish. February 3, 1980, Report by Versar, Inc., Springfield, Virginia in fulfillment of EPA Contract No. 68-01-3852.

29. Perry, D.C., C.C. Chuang, G.A Jungclaus, and J.S. Warner. Identification of Organic Compounds in Industrial Effluent Dischargers. U.S. EPA-560/6-78-009, November, 1978.
30. Keith, L.H., A.W. Garrison, F.R. Allen, M.H. Carter, T.C. Flyd, J.D. Pope, A.D. Thruston, Jr. Identification of Organic Compounds in Drinking Water from Thirteen U.S. Cities. In: Identification and Analysis of Organic Pollutants in Water. L.H. Keith, ed., pp.329-374 Ann Arbor Science Publishers, Ann Arbor, Michigan, 1976.
31. U.S. Environmental Protection Agency. Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, September, 1978.
32. U.S. Environmental Protection Agency. Methods for Organic Chemical analysis of Water and Wastes by GC, HPLC and GC/MS. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 1981.

CHAPTER 13

SAMPLING RADIOACTIVE MATERIALS

13.1 BACKGROUND

Radioactivity in the environment results from the decay processes of individual radionuclides, which are the unstable isotopes of the various chemical elements. Radioactive isotopes possess the same chemical properties as the stable isotopes of a given element. The rules and precautions to be observed for collecting, handling and preserving samples of a specific element or compound apply likewise to its radioactive forms. Guidance given elsewhere in this manual should be reviewed when sampling for radioactive material.

Radioactive waste originates from such diverse nuclear facilities as uranium and thorium mines and mills, fuel enrichment and fabrication plants, nuclear power plants, test reactors, fuel reprocessing plants, waste burial sites, hospitals with nuclear medicine laboratories, nuclear weapons sites, radiochemical producers, research and test laboratories, and manufacturers of products incorporating radioactive substances. Routine gaseous or liquid discharges from nuclear facilities to unrestricted areas contain relatively low concentrations of radioactive material; high level wastes are condensed, sealed and stored on site or transported to radioactive waste disposal sites. The types and amounts of discharged radionuclides vary widely with facility.

The Nuclear Regulatory Commission (NRC) regulates the discharge of radioactive material from nuclear facilities. Concentrations of radionuclides permitted in releases to unrestricted areas are specified in Section 20.106 of 10 CFR 20.(1) The EPA has established permissible concentrations of biologically significant radionuclides in drinking water.(2)

The pathways through which radionuclides in water reach man are shown in Figure 13.1. (3) The drinking water pathway is usually the one that contributes the most dose. Others of significance include consumption of plants and animals that live in water or are fed by irrigation. Less important generally is the external dose received during work or recreational activity from radioactivity in nearby surface water, sediment deposited near shorelines, or irrigated fields. (4)

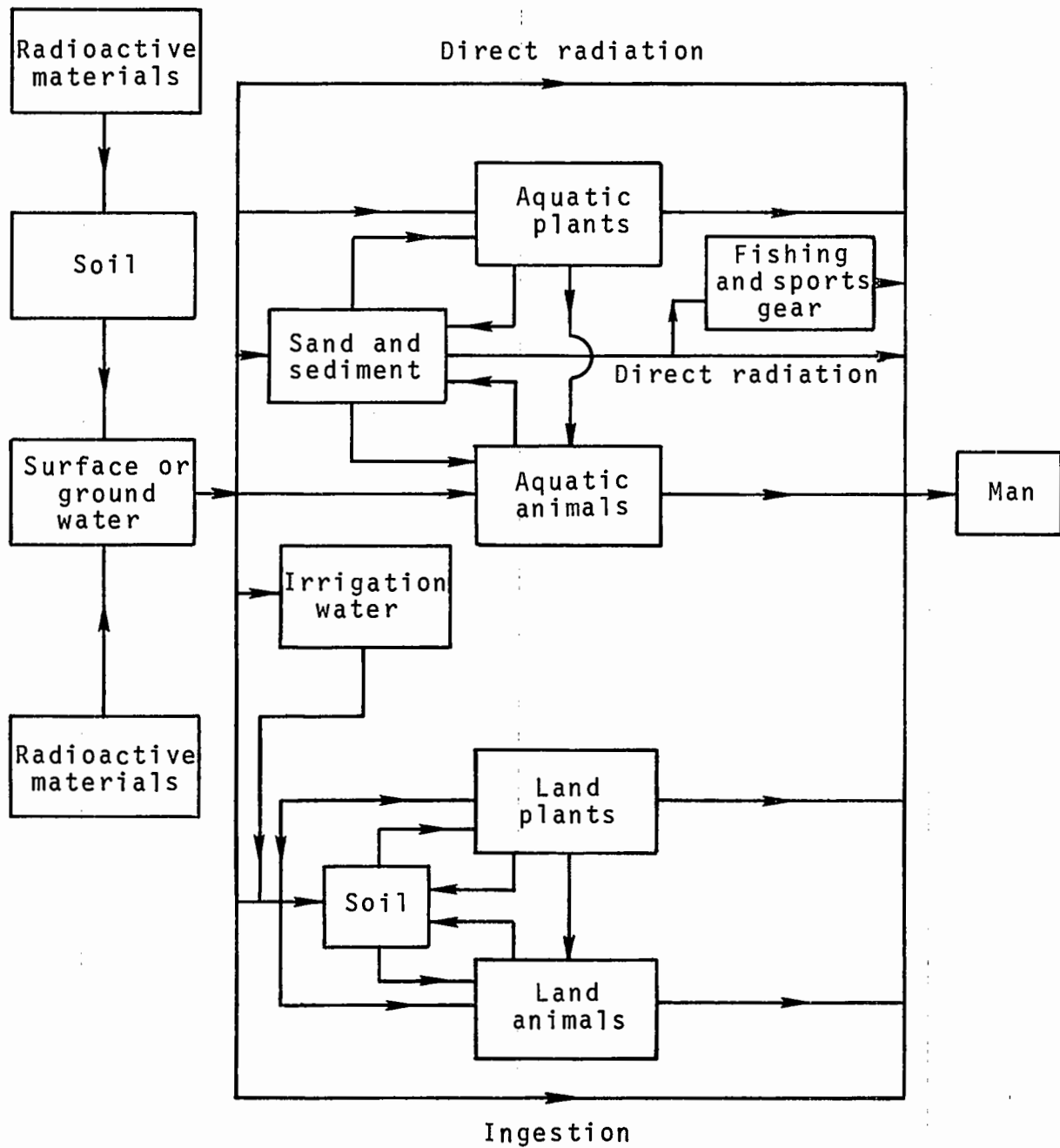


Figure 13.1 Simplified pathways between radioactive materials released to ground or surface waters (including oceans) and man

13.2 GENERAL CONSIDERATIONS

13.2.1 Background Radioactivity

Many naturally-occurring radionuclides exist in soil, water, air and living matter. (5) In addition, man-made radionuclides have become widespread in the natural environment during the past few decades. Due to their presence, background radioactivity at sampling locations must be assessed to determine the actual amount contributed by a nuclear facility to the environment. Control samples taken upstream of the liquid discharge point provide data on the types and amounts of background radionuclides.

In addition, natural and artificial radionuclides occur as impurities in many materials used for sample containers, radiation detection equipment and shields, and chemical reagents. (6) For example, glass contains natural ^{40}K , natural water contains uranium, thorium, and their decay products. Cerium compounds contain thorium. Since these contaminants can produce interferences in radionuclide analyses, their effects must be evaluated before sampling.

13.2.2 Radioactive Decay

The half-lives of sampled radionuclides relative to the interval between sampling and measurement must be considered for determining analytical priority. Those with short (less than one week) half-lives need immediate measurement.

Radionuclide concentrations are reported at levels occurring at the time of sampling. This requires that the times of sampling and analyses be carefully recorded for accurate decay corrections. Note, however, that many naturally occurring radionuclides possess long half-lives which eliminates the need for correction.

References 7, 8, and 9 list half-life values as well as radiation emission data. Reference 9, although comparatively old, provides comprehensive radionuclide data. Many chemistry handbooks provide data pertaining to common radionuclides. Use recent editions since research to obtain more accurate values continues. For this reason, the data used in a analysis must be recorded since the advent of more accurate values may require revision of earlier calculations.

13.2.3 Detection Capability

The ability to identify and measure very low concentrations of radionuclides depends on the types of counting instrumentation on hand and their sensitivity. An important element affecting detection capability is the instrument background level that results from radioactivity ambient in the counting facility and present in the detector shield and the detection equipment itself. Counting equipment presently available together with proper background control provides sufficient sensitivity to measure radionuclides at levels below regulatory standards.

Knowledge of detection capabilities aids in designing the sampling program, such as, necessary sample volume.

Minimum detectable levels for radionuclides frequently observed in water and analyzed by routine techniques are given in Table 13.1 (10) In some cases, several detection limits are listed to show how they vary with method. Gross alpha and beta counting are preferred by some because the instruments are relatively inexpensive and sufficiently sensitive to determine compliance with certain standards such as those for drinking water. Effective use of gross measurements, however, requires knowledge of radionuclide composition.

13.3 FREQUENCY OF SAMPLING

13.3.1 Regulatory

As specified in: 1) license or regulations issued by the NRC or NRC Agreement State; 2) EPA drinking water standards; or 3) permits from other governmental agencies.

13.3.2 Surveillance

Base frequency of sampling on an evaluation of:

1. types, amounts and potential hazards of radionuclides discharged,
2. their behavior in the environment,
3. waste discharge practices,
4. nature of use of local environment, and
5. the distribution and habits of potentially affected populations.(5)

A minimum grab sampling program for surveillance of nuclear power reactors (4) that may be applicable to other types of facilities follows:

1. Surface water -- monthly
2. Ground water, from sources likely to be affected -- quarterly.
3. Drinking water supplies -- sample at the water intake with a continuous flow proportional sampler. If impracticable, obtain a monthly grab sample at the reservoir when its holding time exceeds one month; if less, make sampling frequency equal to reservoir holding time.
4. Sediment -- semi-annually

13.3.3 Other

The frequency for testing effectiveness of waste treatment or control methods is determined by objectives of investigation.

TABLE 13.1 RADIONUCLIDE DETECTION CAPABILITIES

Radionuclide	Physical Half-life	Sample Size, liters	Minimal Detectable Level pCi/liter*	Method
^3H	12.4y	0.008	200	LSC
^{14}C	5730y	0.2	30	LSC
^{60}Co	5.27y	0.4	10	γ -spect (Ge)
		3.5	10	γ -spect (NaI)
^{89}Sr	50.5d	1.0	0.5	CS and LBBC
^{90}Sr	28.5y	1.0	0.2	CS and LBBC
^{131}I	8.04d	2.0	0.1	CS and LBBC
		10.0	0.4	IOR, γ -spect
		0.4	10	γ -spect(Ge)
^{137}Cs	30.0y	0.4	10	γ -spect (Ge)
		1.0	0.3	CS and LBBC
		3.5	10	γ -spect (NaI)
^{226}Ra	1600y	1.0	0.02	RE
^{228}Ra	5.75y	2.0	0.1	CS and LBBC
Ra (total)	--	2.0	0.06	CS and IPC
Gross alpha	--	0.1	0.5	IPC
		0.5	0.1	IPC
Gross beta	--	0.1	2.0	LBBC
		0.5	0.5	LBBC

* Calculated at the 99.7% (three-sigma) confidence level, based on 1000-minute counting intervals and typical counting efficiencies and instrument background levels.

Methods:

CS Chemical separation technique (10)
 IOR Ion-exchange resin
 IPC Internal proportional counter
 LBBC Low background beta counter
 LSC Liquid scintillation counter
 RE Radon emanation and counting by alpha scintillation cell (10)
 γ -spect Gamma-ray spectroscopy, "NaI" denotes a 10 cm x 10 cm NaI (TI) detector and "Ge" an 85 cm³ Ge (Li) detector

13.4 LOCATION OF SAMPLING

Unless specified in regulatory licenses, requirements or permits, selection of proper sampling locations is based on judgment (see Section 13.3.2). As a guide, the EPA recommends for surveillance of light-water reactor sites: (4)

1. Surface water -- At streams receiving liquid waste, collect one sample both upstream and downstream of the discharge point. Obtain downstream sample outside of the restricted area at a location no closer than 10 times the stream width to allow for mixing and dilution. At facility sites on lakes or large bodies of water, sample near but beyond the turbulent area caused by discharge. Record the discharge flow rate at the time of sampling.
2. Drinking water -- Sample all water supplies with intakes downstream and within 10 miles of a nuclear facility. If none exists, sample the first water supply within 100 miles.
3. Ground water -- Monitoring is necessary when a facility discharges radioactive waste to pits or trenches. When local ground water is used for drinking or irrigation, at a minimum, sample the nearest affected well. Subsurface movement of most radionuclides is retarded by the filtering and ion-exchange capacity of soil; tritium, however, moves more rapidly than most radionuclides.
4. Sediment -- Samples to detect accumulation of undissolved or adsorbed radionuclides in beds of streams or other bodies of water receiving liquid effluents from nuclear facilities are collected: 1) downstream near the discharge outfall but beyond the turbulent area; 2) downstream of the discharge at locations where sediment is observed to accumulate, such as at bends of streams or dam impoundments; and 3) upstream near the discharge outfall but beyond its influence, to determine background radionuclides.

See also Section 8.4 of this manual for additional guidance in selecting proper sample locations.

13.5 SAMPLE VOLUME

Determining necessary sample volume depends on the types and number of analyses to be performed and the sensitivity of available analytical instruments. For surveillance purposes, obtain the following minimum volumes:

Measurement	Volume, liters
Gamma-ray spectroscopy (NaI detector)	3.5*
Gamma-ray spectroscopy (GeLi detector)	0.4
Gross alpha or beta only	0.1
Liquid scintillation - tritium only	0.01

* Water can be subsequently used for analyses requiring chemical separations (e.g., ^{89}Sr , ^{90}Sr).

Sediment analyses usually require 1 kg. of sample. (5)

Increase the volumes or weights when sample splitting or replicate analyses is required for quality control purposes.

13.6 SAMPLE CONTAINERS

Use sample containers that minimize radionuclide losses by adsorption or other processes during collection and storage. Containers made of fluorinated hydrocarbon material (e.g. Teflon) are preferred because of their resistance to adsorption. Polyethylene and polyvinyl chloride are also recommended.(11) Glass and metal containers tend to retain radionuclides.(12) Glass bottles also are more subject to breakage during handling.

When adsorption problems persist, wash containers and sampling apparatus with HCl or HNO_3 before sampling or flush the containers and apparatus with the liquid to be collected before final sampling.(13) Test for adsorption by analyzing used containers by gamma-ray spectroscopy when this type of radionuclide emission is present. For other emitters, use successive acid leachings with hot aqua regia and analyze the leachate.(12)

Discard containers after use to eliminate possibility of cross-contamination through re-usage. If for economic reasons the more expensive containers must be used again, test for adsorbed contamination as described above.

13.7 SAMPLE FILTRATION

Filter water and wastewater sample to segregate liquid and solids when the radionuclide contents are to be determined in either or both the suspended solids and dissolved matter fractions. Filter as soon as practicable after collection to assure that no redistribution occurs during storage before analysis.(12) Use membrane or glass fiber filters since these types resist adsorption effects.(11) Filter before adding preservative or other substances to the sample since they can effect changes in distribution.(14)

13.8 SAMPLE PRESERVATION

Radionuclides are subject to many little understood chemical and physical processes at the very low concentrations (parts per billion or less), which are typical of most environmental water samples.(11)(12)(15) Variations in original sample concentration or homogeneity can result from: 1) adsorption on sampling apparatus, container walls or solid material in the sample;(5) 2) co-precipitation of radionuclides due to precipitation of Fe and Mn in ground water samples exposed to air;(15) 3) ionic exchange with components of glass containers;(12) 4) uptake by bacteria, algae or other biological matter in the sample;(13) and 5) formation of colloids.(12) Many of these problems are thought to occur because the amounts of stable isotopes are insufficient to serve as a carrier for the radioactive nuclides of the same element.(11)

The standard preservation technique for radionuclides in water and wastewater samples is acidification to a pH of < 2 with HCl or HNO₃.(14)(15) Several exceptions exist:

1. Tritium - add no acid; begin analysis immediately upon return to the laboratory.(10)
2. Carbon 14 - see tritium
3. Radiocesiums - use HCl only
4. Radioiodines - see tritium: acid oxidizes iodides to iodines which are rapidly lost through volatilization.(12) For samples containing ³H, ¹⁴C or ¹³¹I along with radionuclides requiring preservatives, obtain duplicate samples and add acid to only one.

Add acid preservative after sample collection (but not before filtration - see Section 13.7) or as soon as practicable but do not delay beyond five days.(14)

When acid preservation is not desirable: 1) add isotopic carriers of the same elements as the radionuclides;(12) 2) refrigerate samples at or near their freezing temperature to retard chemical reaction rates and to inhibit bacterial growth.(16)

13.9 GENERAL SAMPLING PROCEDURE - WATER AND WASTEWATER

The following procedure summarizes the elements of good practice for collecting and preserving samples of water and wastewater for radionuclide measurements. These guidelines apply to the situation where no unusual circumstances exist:

1. Flush sample lines, equipment or other apparatus and sample container with sample medium to minimize adsorption effects. Use type of containers recommended in Section 13.6.
2. Avoid floating debris and bottom sediments when sampling surface waters. When aliquoting large samples containing significant amounts of suspended solids, vigorously shake or mix to assure

- representative subsamples.
3. Wash sampling apparatus with distilled water to minimize contamination of subsequent samples.
 4. Filter sample as soon as practicable after collection when radionuclide distribution in soluble and/or insoluble phases is to be determined (see Section 13.7). Use membrane or glass fiber filters.
 5. Add preservative of the required type to liquid samples (see Section 13.8). When concentrated HCl or HNO₃ is the indicated type, add to obtain a pH of < 2. In cases of mixtures of radionuclides, for some (³H, ¹⁴C, ¹³¹I) of which acid preservation is not recommended, collect replicate samples and treat only one with acid.
 6. Seal sample container tightly. Complete sample data label including time of collection for decay corrections.
 7. Analyze samples containing short-lived radionuclides as soon as possible.
 8. Discard sample containers after use or test for contamination if expensive types of containers are to be used again.

13.10 RADIATION SAFETY

Storage of large numbers or volumes of samples containing radioactivity is a potential source of exposure to workers occupying the area. However, this is unlikely with environmental samples due to low radionuclide content. If in doubt, survey the area periodically with a beta-gamma survey instrument, such as a Geiger-Mueller (GM) meter. Note that sample containers reduce all alpha-particle and much beta-particle radiation. If radiation levels above instrument background occur at work stations, consult a radiation safety specialist for procedures to reduce exposure levels and for proper disposal techniques when samples are no longer needed.

13.11 REFERENCES

1. U.S. Nuclear Regulatory Commission. Standards for Protection Against Radiation. Title 10, Code of Federal Regulations, Part 20, Federal Register, U.S. Government Printing Office, Washington, D.C. 1975.
2. Office of Water Supply, U.S. Environmental Protection Agency. National Interim Primary Drinking Water Regulation. EPA-570/9-76-003, U.S. Government Printing Office, Washington, D.C., 1977.
3. Report by Committee 4 of the International Commission on Radiological Protection. Principles of Environmental Monitoring related to the Handling of Radioactive Materials. ICRP Publication 7, Pergamon Press, Oxford, 1965.

4. U.S. Environmental Protection Agency, Office of Radiation Programs. Environmental Radioactivity Surveillance Guide. EPA report No. ORP/SID 72-2, 1972.
5. National Council on Radiation Protection and Measurements. Environmental Radiation Measurements. NCRP Report No. 50, 1976.
6. DeVoe, J.R. Radioactive Contamination of Materials Used in Scientific Research. National Academy of Sciences - National Research Council, Nuclear Science Series Report No. 34, 1961.
7. Martin, M.J., editor, Nuclear Decay Data for Selected Radionuclides. Oak Ridge National Laboratory, ORNL-5114, March 1976.
8. Martin, M.J. and P.H. Blichert-Toft. Radioactive Atoms. Nuclear Data Tables A8, Nos. 1-2, 1970.
9. Lederer, C.M., J.M. Hollander, and I. Perlman. Table of Isotopes. John Wiley, New York, 1967.
10. Krieger, H.L. Interim Radiochemical Methodology for Drinking Water. U.S. Environmental Protection Agency, Report No. EPA-600/4-75-008 (Revised), March 1976.
11. Mitchell, N.T. Manual on Analysis for Water Pollution Control. Radiological Examination. World Health Organization, to be published.
12. Kahn, B. Determination of Radioactive Nuclides in Water. Water Pollution Control Handbook, L.L. Ciaccio, ed., Marcel Dekker, Inc., New York, 1973.
13. Corley, J.P., D.H. Denham, D.E. Michels, A.R. Olsen and D.A. Waite. A Guide for Environmental Radiological Surveillance at ERDA Installations. U.S. Energy Research & Development Administration, Report No. ERDA 77-24, March, 1977.
14. American Public Health Association. Standard Methods for the Examination of Water and Wastewater. 14th edition, Washington, D.C., 1976.
15. Thatcher, L.L., V.J. Janzer and K.W. Edward. Methods for Determination of Radioactive Substances in Water and Fluvial Sediments (Chapter A5, Book 5, Techniques of Water-Resources Investigations of the United States Geological Survey. U.S. Government Printing Office, Washington, D.C. 1977.
16. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory. Methods for Chemical Analysis of Water and Wastes. EPA Report No. EPA-625/6-74-003a, 1974.

CHAPTER 14

COLLECTING AND HANDLING MICROBIOLOGICAL SAMPLES

14.1 BACKGROUND

Fecal contamination from warm-blooded animals and man is present in certain industrial effluents, urban and rural run-off, and in municipal wastewaters. It can cause serious diseases and other health problems in drinking water supplies and in recreational, agricultural, or processing waters used in the food, dairy and beverage industries. Consequently, the Federal Water Pollution Control Act Amendments (Clean Water Act), the Marine Protection, Research and Sanctuaries Act (Ocean Dumping Act), and the Safe Drinking Water Act, require monitoring of water supplies, ambient waters and wastewater effluents for compliance with bacterial limits. (1)(2)(3)

To control pathogens discharged into these waters, selected groups of microorganisms are monitored as indicators of the sanitary quality of a stream or water supply. These include "total" bacteria (standard plate count), total coliform bacteria, fecal coliform bacteria, and fecal streptococci. The pathogens Salmonella, Shigella, Giardia, Pseudomonas, Klebsiella, Clostridium spp, and viruses, are not routinely tested because they are present in such small numbers that the methodology is cumbersome, time-consuming and seldom quantitative.

14.2 ANALYTICAL METHODOLOGY

The bacterial parameters: Standard Plate Count, Total Coliform, Fecal Coliform, Fecal Streptococci and Salmonella will be discussed.

For a more detailed description of the methodologies see Standard Methods and the EPA microbiological manual.(4)(5) The specific analytical methodologies required for compliance monitoring of drinking water, and wastewater discharges are described in the regulations.

14.2.1 Standard Plate Count

The Standard Plate Count (SPC) Method is a direct quantitative measurement of the viable aerobic and facultative anaerobic bacteria in a water environment, that are capable of growth on the plating medium. This test is usually performed by suspension of the sample in agar with subsequent growth and counting of colonies (pour plate). The counts may also be obtained from surface growth colonies on a spread plate or on a

membrane filter. Although no one set of plate count conditions can enumerate all organisms present, the Standard Plate Count Method provides the uniform technique required for comparative testing and for monitoring water quality in selected applications.

The Standard Plate Count is a useful tool for determining the bacterial density of potable waters for quality control studies of water treatment processes. It provides a method for monitoring changes in the bacteriological quality of finished water throughout a distribution system to indicate the effectiveness of chlorine in the system as well as the possible existence of cross-connections, sediment accumulations and other problems within the distribution lines. The procedure may also be used to monitor quality changes in bottled water or emergency water supplies.

14.2.2 Coliforms

The coliform or total coliform group includes all of the aerobic and facultative anaerobic, gram negative, nonspore-forming, rod-shaped bacteria that ferment lactose in 24 to 48 hours at 35° in a multiple tube most probable number (MPN) procedure, or that produce a golden green metallic sheen within 24 hours at 35°C in the membrane filter (MF) procedure. The definition include the genera: Escherichia, Citrobacter, Enterobacter, and Klebsiella.

The coliform group may be subdivided into the two following categories:

1. Coliforms normally of fecal origin (primarily Escherichia coli types).
2. Coliforms usually associated with vegetation and soils (Citrobacter, Enterobacter, Klebsiella, and Escherichia spp), which may occur in fecal matter but in smaller numbers than E. coli.

The two analytical techniques recommended by EPA and Standard Methods for enumeration of coliforms are the Most Probable Number (MPN), and the Single-Step, Two-Step and Delayed Incubation Membrane Filter methods.(4)(5)

Microbiological standards for public water supplies and drinking waters are based on total coliform numbers which include coliforms from sources other than human and animal feces.

14.2.3 Fecal Coliforms

The trend in recent years is to obtain a more accurate estimate of the sanitary quality of the ambient and wastewater by conducting fecal coliform analyses.

The fecal coliform bacteria are part of the total coliform group. They are normally inhabitants of the gut of warm blooded animals and hence are tolerant of higher temperatures than other coliforms. The fecal

coliform group are defined as gram negative nonspore-forming rods that ferment lactose in $24 \pm$ two hours at $44.5 \pm 0.2^{\circ}\text{C}$ with the production of gas in the multiple tube procedure, or that produce acidity indicated by blue colonies in the membrane filter procedure.

The major species in the fecal coliform group is Escherichia coli. It is indicative of fecal pollution and of the possible presence of enteric pathogens. No method is presently available which distinguishes human fecal coliforms from those of other warm-blooded animals.

The analytical techniques for identifying fecal coliforms in water are the direct MF, the delayed incubation MF, and the multiple tube, MPN methods.

Both the MF and MPN fecal coliform tests are applicable to the examination of lakes and reservoirs, wells and springs, public water supplies, natural bathing waters, secondary non chlorinated effluents from sewage treatment plants, farm ponds, storm water runoff, raw municipal sewage, and feedlot runoff. The MF test has been used with varied success in marine waters.

14.2.4 Fecal Streptococci

The fecal streptococci, can be used to indicate the sanitary quality of water and wastewater. The group includes the serological groups D and Q: Streptococcus faecalis, S. faecalis subsp. liquifaciens, S. faecalis subsp. zymogenes, S. faecium, S. bovis, S. equinus, and S. avium.

The MF, MPN and direct pour plate procedures can be used to enumerate and identify fecal streptococci in water and wastewater.

Positive fecal streptococci results verify fecal pollution and may provide additional information concerning the recency and probable origin of pollution, when used as a supplement to fecal coliform analyses. They are not known to multiply in the environment.

Speciation of streptococci in the sample may be obtained by biochemical characterization. Such information is useful for source investigations.

14.2.5 Salmonella

The genus, Salmonella, is comprised of a large number of serologically related, gram negative, non-spore forming bacilli that are pathogenic for warm blooded animals including man, and which are found in reptiles, amphibians and mammals. They cause enteritis and enteric fevers through contaminated water, food or food products. Because Salmonella are responsible for many outbreaks of waterborne disease, increased efforts have been made to identify and enumerate them.

Generally the numbers of Salmonella present in water or wastewater are

very low, so that sample volumes larger than a liter are required to isolate this pathogen. Because of the lower numbers of Salmonella in water, negative results do not assure absence of Salmonella and analyses for indicator organisms are usually run concurrently to measure the potential health risk.

Recommended methods for recovery and identification of Salmonella from water and wastewater are presented in Standard Methods and the EPA Manual.(4)(5) The methods are particularly useful for recreational and shellfish harvesting waters. No single method of recovery and identification of these organisms from waters and wastewaters is appropriate for all sampling situations. Rather the method is selected based on the characteristics of the sample and microbiologist's experience with the procedures. Multiple option techniques are described for sample concentration, enrichment, isolation and identification.

14.2.6 Enteric Viruses (4)

Viruses excreted by animal and man are present in domestic sewage after waste treatment and enter streams and lakes that serve as the source of drinking water supplies for many communities. Viruses are excreted in much lower numbers than coliform bacteria, and do not multiply outside of the animal or human host. Dilution in ambient waters, sewage treatment, and water treatment further reduces viral numbers in the environment. However, it has been demonstrated that infection can be produced by a few viral units.

Sample concentration is needed to demonstrate and quantitate viruses in clean or potable waters because the numbers are very low. For clean waters, 400 liters or more of water must be sampled. The most promising method for concentrating small quantities of viruses from those waters is adsorption onto a microporous filter. Viruses are removed from the filter with a protein eluant or glycine buffer at a controlled pH. Viruses may be concentrated a second time.

Measuring viruses in wastewaters and natural waters is even more difficult because of the suspended solids present. For such samples, the aqueous polymer two-phase separation technique may be used directly for virus recovery but the sample size is limited to two-four liters.

After concentration of viruses and elution, the eluate is analyzed by cell culture or whole animal assay.

At this time, the routine examination of the waters and wastewaters for enteric viruses is not recommended. However, for special needs such as wastewater reuse, disease control, or special studies, virus testing can be done but only by qualified virologists with proper facilities.

14.3 SAMPLE BOTTLE PREPARATION (4)(5)

Sample bottles must be resistant to sterilizing conditions and the

solvent action of the water. Wide-mouth glass or heat-resistant plastic bottles with screw-cap or ground-glass stoppers may be used if they can be sterilized without producing toxic materials. See Figure 14.1. Screw-capped bottles must be equipped with neoprene rubber liners or other materials that do not produce bacteriostatic or nutritive compounds upon sterilization.

14.3.1 Selection and Cleansing of Bottles

Select bottles of sufficient capacity to provide a volume necessary for all analyses anticipated. Use at least a 125 mL bottle for a minimum sample volume of 100 mL and to provide adequate mixing space. Discard bottles which have chips, cracks, and etched surfaces. Bottle closures must produce a water-tight seal. Before use, thoroughly clean bottles and closures with detergent and hot water and rinse with hot water to remove all traces of detergent. Then rinse three times with a good quality laboratory reagent water. A test for bacteriostatic or inhibitory residues on glassware is described in Standard Methods and in EPA's Manual. (4)(5)

14.3.2 Use of Dechlorinating and Chelating Agents

Use a dechlorinating agent in the sample bottle when water and wastewater samples containing residual chlorine are anticipated. Add 0.1 mL of a 10 percent solution of sodium thiosulfate to each 125 mL (4 oz.) sample bottle prior to sterilization.

Use a chelating agent when waters are suspected of containing more than 0.01 mg/L concentration of heavy metals such as copper, nickel, zinc, etc. Add 0.3 mL of a 15 percent solution ethylenediamine tetraacetic acid, tetra-sodium salt (EDTA), to each 125 mL (4 oz.) sample bottle prior to sterilization. (6)(7)

14.3.3 Wrapping of Bottles

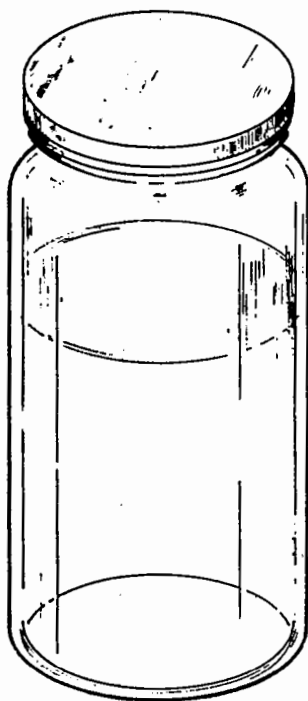
Protect the tops and necks of glass-stopper bottles from contamination by covering them with aluminum foil or kraft paper before sterilization. Screw cap closures do not require a cover.

14.3.4 Sterilization of Bottles

Autoclave glass or heat resistant polypropylene plastic bottles at 121°C for 15 minutes. Glassware may be sterilized in a hot air oven at 170°C for two hours. Ethylene oxide gas sterilization is acceptable for plastic containers which are not heat resistant. Before use of sample bottles sterilized by gas, store overnight to allow the last traces of gas to dissipate.

14.4 SAMPLING METHODS AND EQUIPMENT (5)

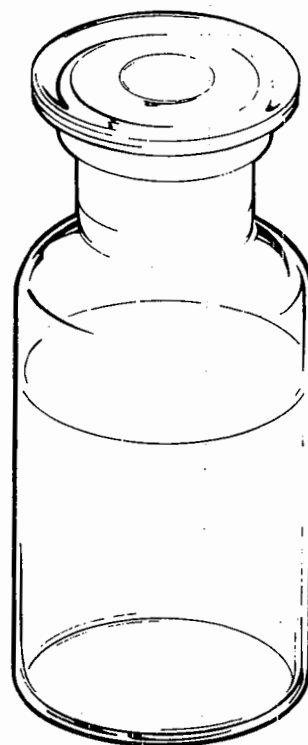
These methods are applicable for sampling potable water, streams and rivers, recreational waters such as bathing beaches and swimming pools,



Screw-cap Glass or
Plastic Bottle



Plastic Bag (Whirl-pak)



Glass Stoppered
Bottle

Figure 14.1 Suggested Sample Containers

lakes and reservoirs, public water supplies, marine and estuarine waters, shellfish harvesting waters, and domestic and industrial waste discharges.

In no case should composite samples be collected for microbiological examination. Data from individual samples show a range of values which composite samples will not display. Individual results give information about industrial process variations. Also, one or more portions that make up a composite sample may contain toxic or nutritive material and cause erroneous results.

Do not rinse bottle with sample, but fill it directly to within 2.5 - 5 cm (1 - 2 in.) from the top to allow mixing of the sample before analysis. Use caution to avoid contaminating the sample with fingers, gloves or other materials. Test any chlorinated sample for absence of chlorine, to assure that the naturalizing agent (14.3.2) was effective.

Completely identify the sampling site on a field log sheet, label, and on a chain of custody tag, if this is required. See Chapter 15.

14.4.1 Tap Sampling

Do not collect samples from spigots that leak or that contain aeration devices or screens. In sampling direct connections to a water main, flush the spigot for 3 to 5 minutes at moderate flow to clear the service line. For wells equipped with hand or mechanical pumps, run the water to waste for 3 to 5 minutes at a moderate flow before the sample is collected. Remove the cap aseptically from the sample bottle. Hold the sample bottle upright near the base while it is being filled. Avoid splashing. Replace bottle closure and hood covering.

14.4.2 Surface Sampling By Hand

Collect a grab sample directly into a sample bottle prepared as described in Section 14.3. Remove the bottle top cover and closure and protect them from contamination. Avoid touching the inside of the closure. Grasp the bottle securely at the base with one hand and plunge it mouth down into the water, avoiding surface scum. Position the bottle towards the current flow and away from the hand of the collector, the shore, the side of sampling platform, or boat. See Figure 14.2. The sampling depth should be 15 to 30 cm (6 to 12 in.) below the water surface. If the water body is static, an artificial current can be created by moving the bottle horizontally in the direction it is pointed and away from the sampler. Tip the bottle slightly upwards to allow air to exit and the bottle to fill. After removal of the bottle from the stream, tightly stopper and label the bottle.

14.4.3 Surface And Well Sampling By Weighted Bottle Frame

When sampling from a bridge or other structure above a body of water, place the bottle in a weighted frame that holds the bottle securely. See Figure 14.3. Remove the cover and lower the device to the water. It is preferable to use nylon rope which does not absorb water and will not rot.

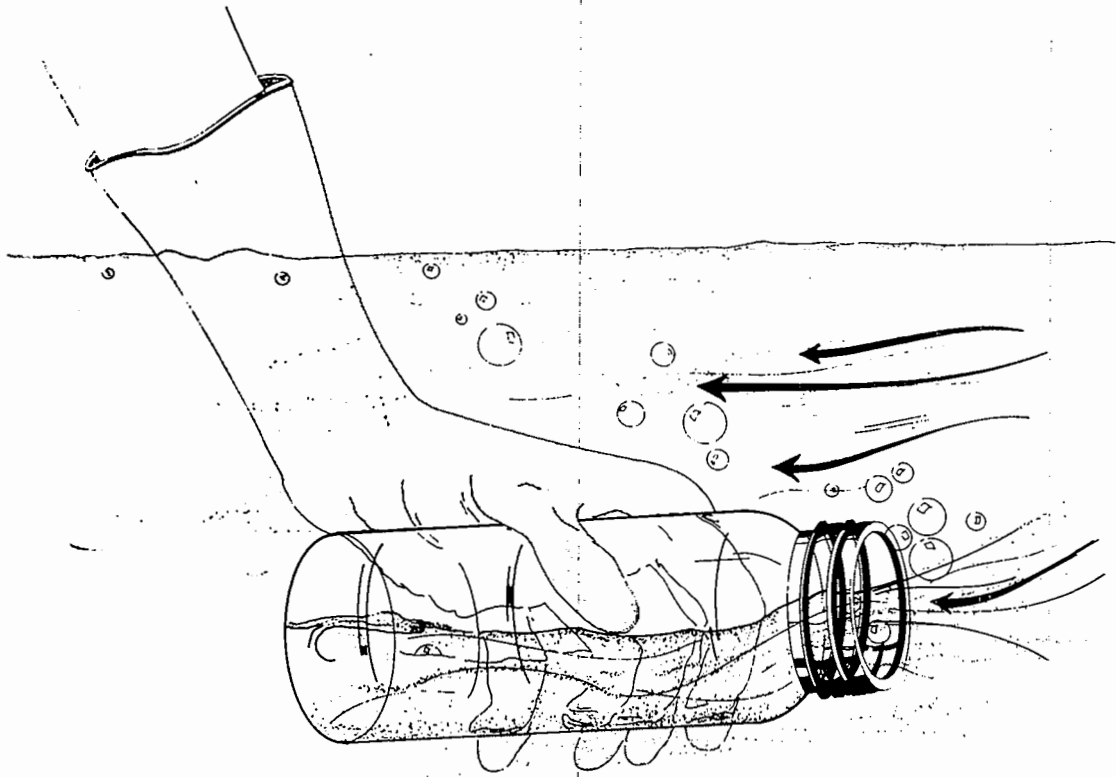


Figure 14.2 Demonstration of Technique Used in Grab Sampling of Waters and Wastewaters

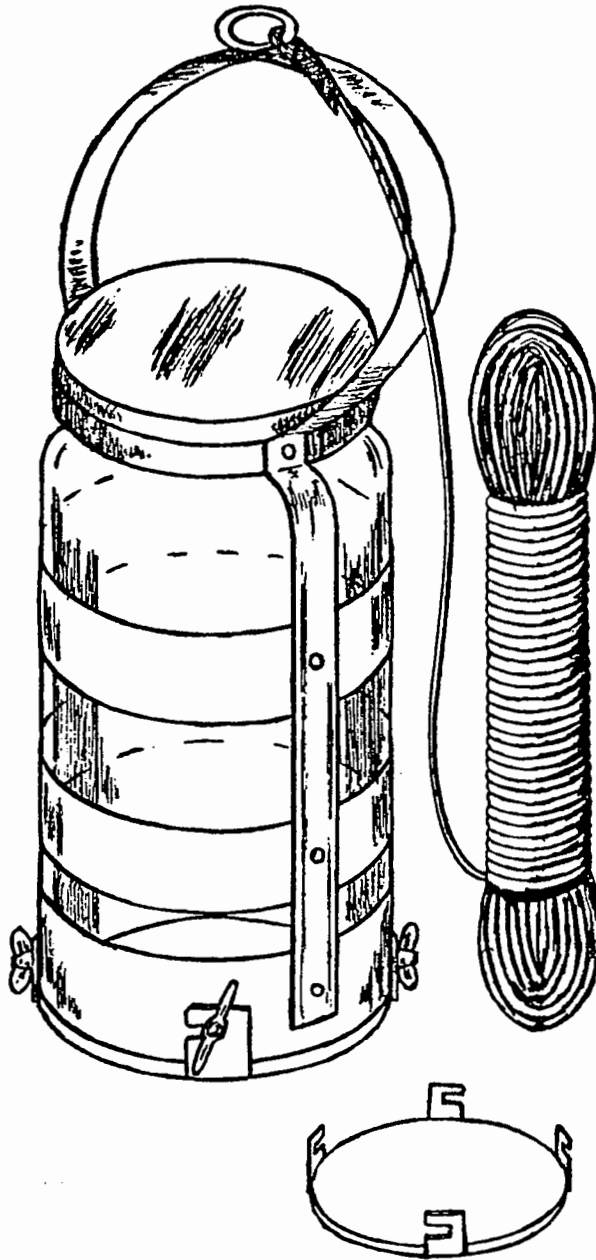


Figure 14.3 Weighted Bottle Frame and Sample Bottle for Grab Sampling

Swing the sampling device downstream, and then allow it to drop into the water, while pulling on the rope so as to direct the bottle upstream. Pull the sample device rapidly upstream and out of the water, simulating the scooping motion of grab sampling. Take care not to dislodge dirt or other material from the sampling platform.

Use a weighted sterilized sample bottle when sampling a well that does not have pumping machinery. Avoid contaminating the sample with surface scum or dislodged material from the sides of the well.

14.4.4 Depth Sampling

Several additional devices are needed for collection of depth samples from lakes, reservoirs, estuaries and the oceans. These depth samplers require lowering the sample device and/or container to the desired depth, then opening, filling, and closing the container and returning the device to the surface. Although depth measurements are best made with a pre-marked steel cable, the sample depths can be determined by pre-measuring and marking a nylon rope at intervals with non smearing ink, paint, or fingernail polish. The following list of depth samplers is not inclusive but can serve as a guide: The ZoBell J-Z, the Niskin, the New York Dept. of Health, and the Kemmerer samplers. See Figures 14.4, 14.5, 14.6 and 14.7.

14.4.5 Sediments And Sludge Sampling

Microorganisms attach to particles and artifacts in water and are found in large numbers in the bottom sediment and at interfaces in any body of water. Sewage solids in treated domestic wastewaters and sludges contain very large numbers of microorganisms which pass into receiving streams, lakes and oceans and then settle into the bottom sediments. This is a particular concern in the ocean dumping program because of the concentrated disposal of very large amounts of sludge in selected ocean dump sites. Microorganisms in these materials are periodically released into the overlying waters as the bottoms are disturbed.

Sediments and bottom materials are difficult to sample because of the variable composition, size, density and shape of particles and the lack of homogeneity. They vary from light, fluffy particles to compacted high density, solid layers.

Grab samples are not usually satisfactory for quantitative bottom sampling because they may contain material which is not representative. However, they give an indication of the processes that occur.

Corers are used in quantitative work though none is entirely satisfactory. The Ekman corer is used when sampling from small boats. The Wildlife Co. (Saginaw, Michigan) coring device is used in shallow water (15 meters or less). In extremely shallow water a lucite tube can be inserted into the sediment by hand, and capped by a stopper. The Van Donsel-Geldreich sampler can be used to collect soft sediments or muds in relatively deep waters. It uses a sterile plastic bag in a weighted frame

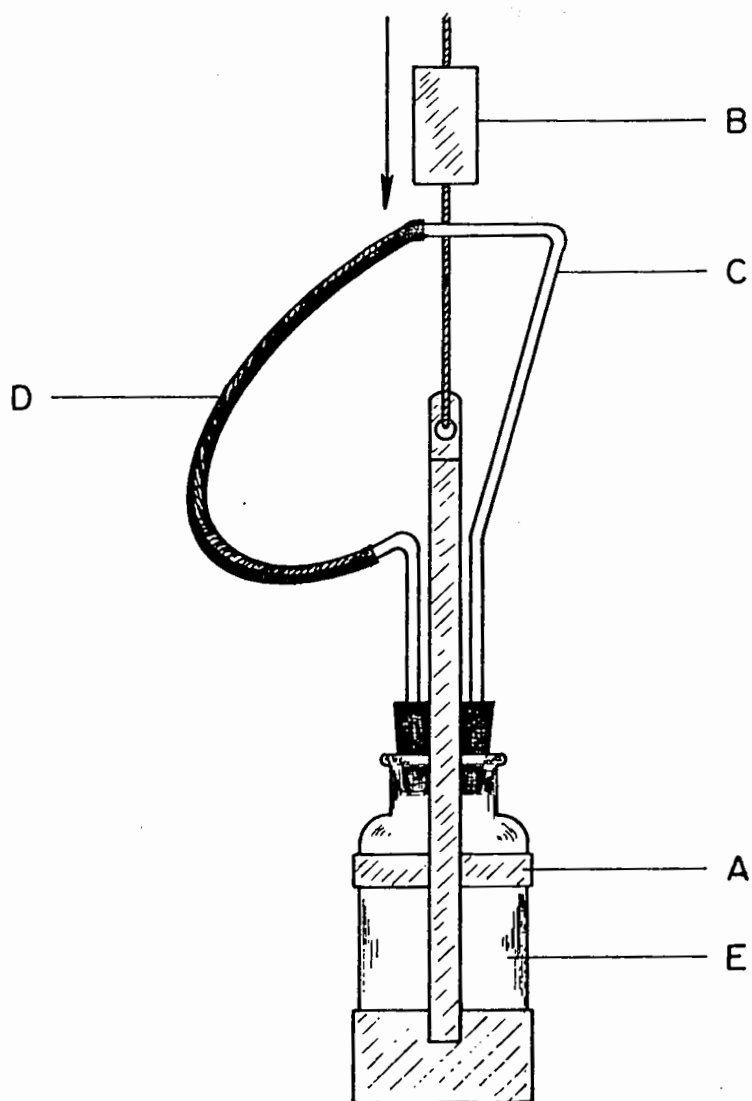


Figure 14.4 Zobell J-Z Sampler. (A) metal frame, (B) messenger, (C) glass tube, (D) rubber tube and (E) sterile sample bottle

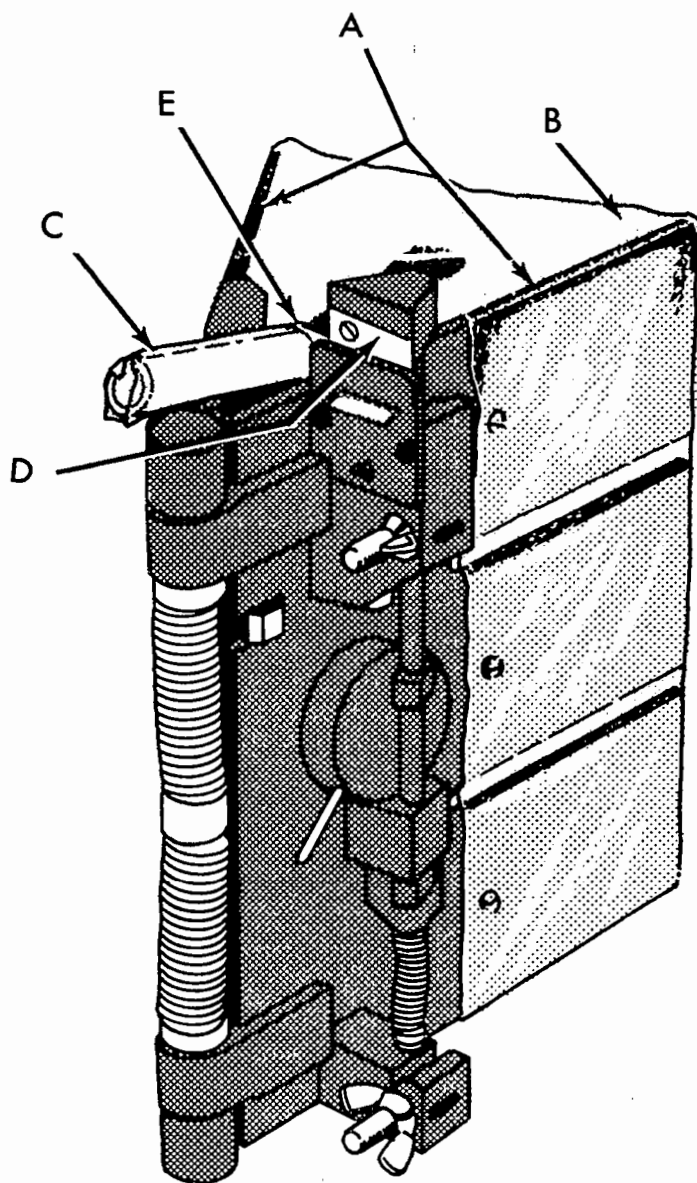


Figure 14.5 Niskin Depth Sampler. (A) hinged plates, (B) plastic bag, (C) plastic filler tube in sheath, (D) guillotine knife and (E) closure clamp.

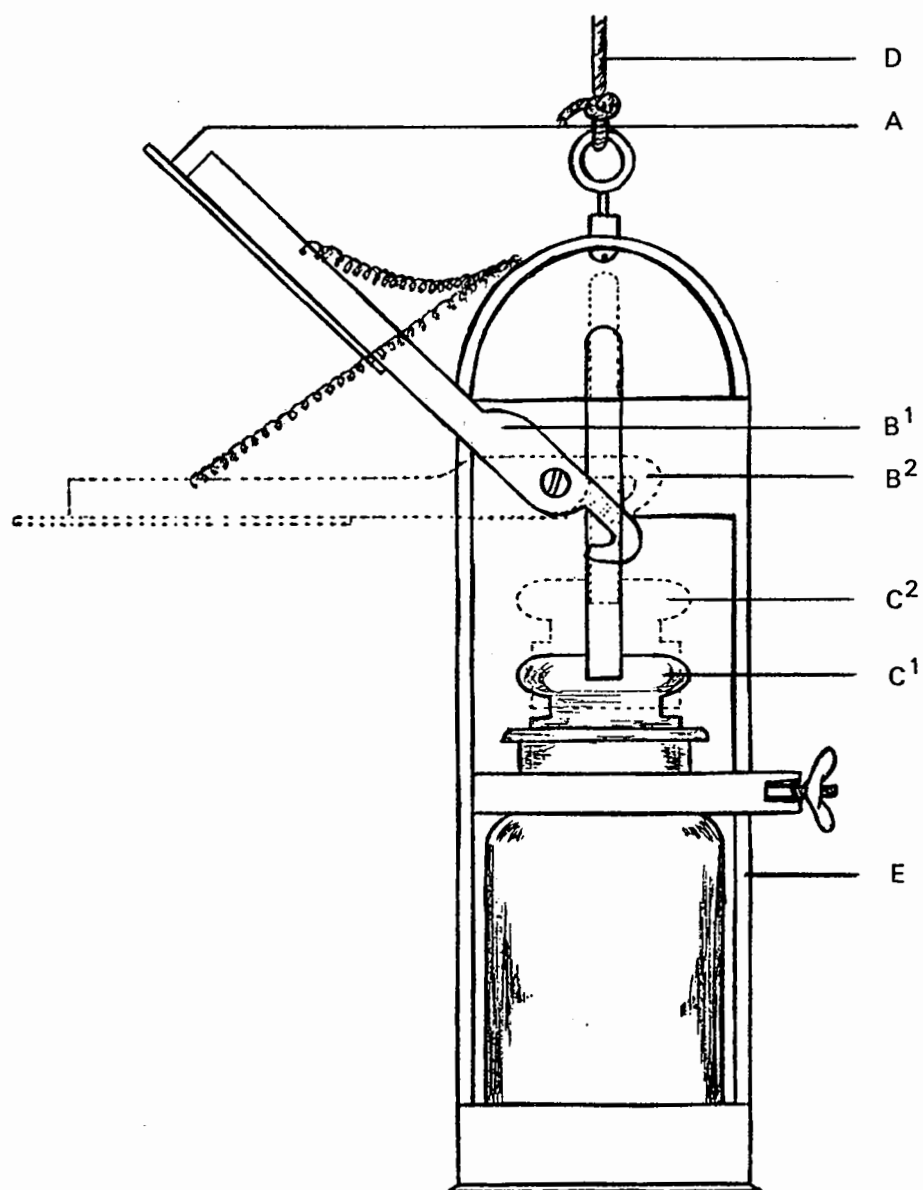


Figure 14.6 New York State Dept. of Health Depth Sampler. (A) vane, (B¹) lever in closed position, (B²) lever in open position, (C¹) glass stopper in closed position, (C²) glass stopper in open position, (D) suspension line, and (E) metal frame.

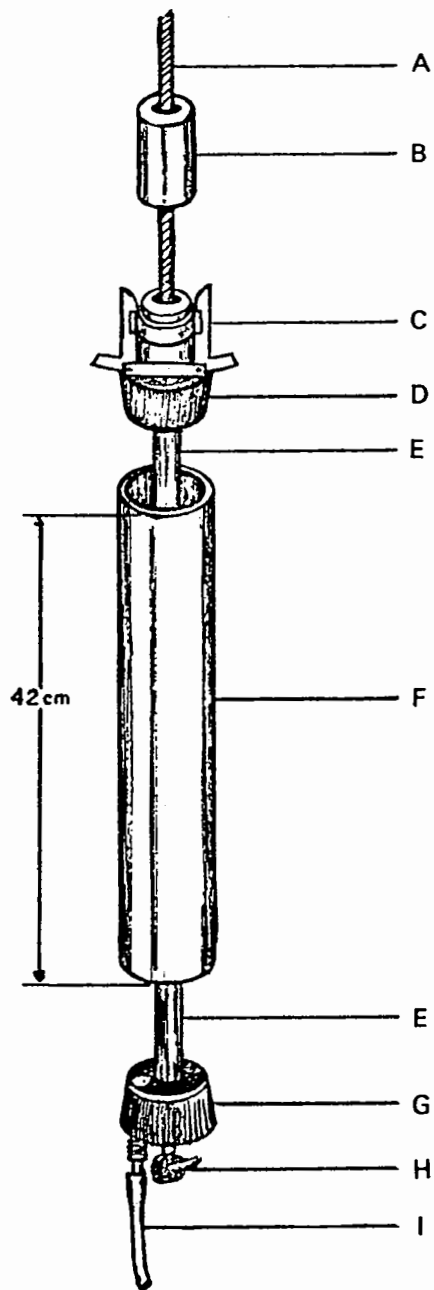


Figure 14.7 Kemmerer Depth Sampler. (A)nylon line, (B)messenger, (C)catch set so that the sampler is open, (D)top rubber valve, (E)connecting rod between the valves, (F)tube body, (G)bottom rubber valve, (H)knot at the bottom of the suspension line and, (I) rubber tubing attached to the spring loaded check valve.

to collect the sample and then closes the bag with a wire loop. See Figure 14.8.

14.5 SAMPLE FREQUENCY AND SITE SELECTION (5)

14.5.1 Frequency of Sampling

The frequency of sampling depends upon the type of pollution that is to be measured. Cyclic pollution and its duration are measured as frequently as practical immediately downstream from the source. Uniform pollution loads are measured at greater distances downstream from the source and at less frequent time intervals than cyclic pollution. A common approach for short term studies is to collect samples from each site daily and advance the sampling intervals one hour during each 24 hour period to obtain data for a 7 to 10 day study.

Often the numbers of samples to be collected are specified by NPDES permits, drinking water regulations, or by State requirements. Some standards require a minimum number of samples to be collected each month. Other standards are less explicit and simply indicate that the geometric mean coliform density shall not exceed a certain level each month, with no more than 10%, 20%, etc. of samples exceeding a certain value. Where the number of samples required is undetermined, a sufficient number should be collected to measure the variations in conditions.

14.5.2 Raw Water Supplies

Reservoirs and lakes used as water supplies are sampled at inlets, other possible sources of pollution, the draw off point, the quarter point intervals around the draw off point at about the same depth, and the reservoir outlet.

14.5.3 Potable Water Supplies

Coliform standards for potable water supplies established by Public Health Service Act of 1962 were amended by The Safe Drinking Water Act of 1974 (SDWA) and its supporting regulations.(3)(8) The levels for the 1962 PHS Standards were retained in the SDWA but were redefined as Maximum Contaminant Levels (MCLs). As with the previous standards, the MCLs emphasize the importance of collecting samples at regular intervals, in numbers proportionate to the population served, and at points representative of conditions in the distribution system. A set protocol was established for repeat sampling when positive coliform results occur. For application of the MCLs, the frequency of sampling and the location of sampling points is established jointly by the utility, the Reporting Agency, and the Certifying Authority.

The SDWA also specifies that any laboratory generating data for public water supplies, as required under the Act, must be certified according to the procedures and criteria in the Laboratory Certification Manual.(9) The

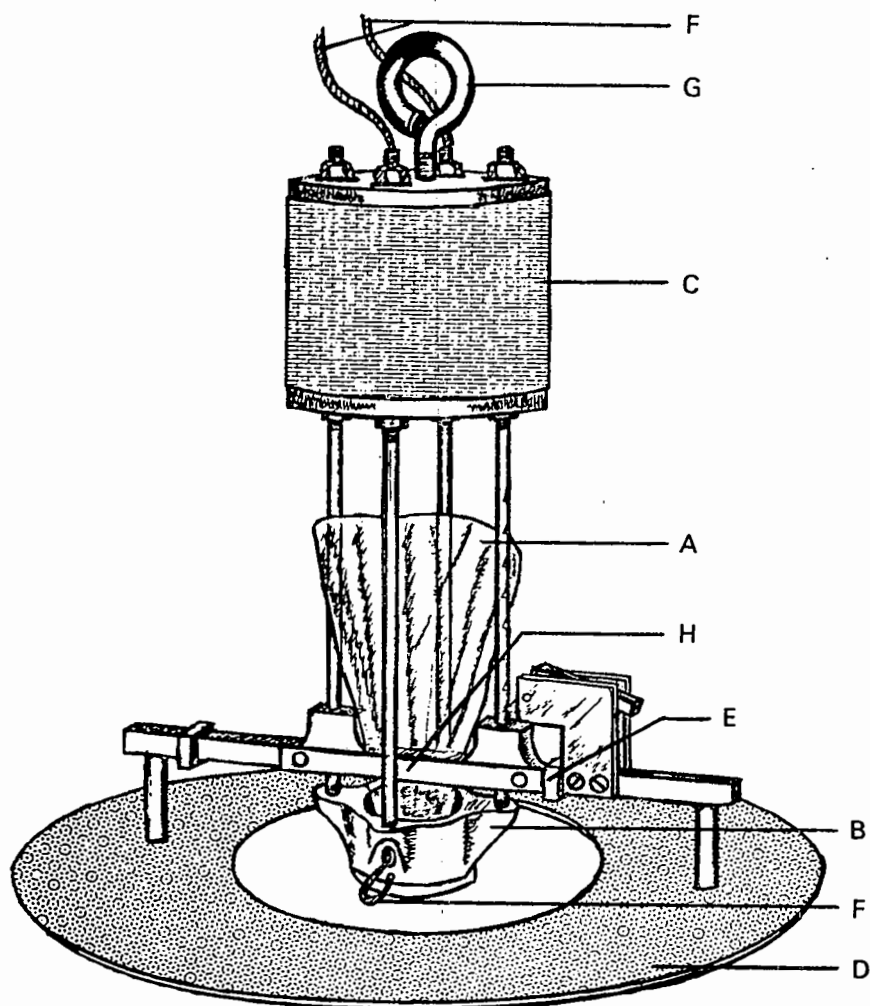


Figure 14.8 VanDonsel-Geldreich Sediment Sampler. (A)sterile "Whirl-Pak" plastic bag, (B)nose piece, (C)weight, (D)mud plate, (E)slide bar, (F)part of the double noose, (G)attachment for the suspension line and (H)bag clamp bar.

laboratory facility, personnel, equipment and instrumentation, sampling methodology, quality control, data reporting and necessary action responses are specified.

14.5.4 Distribution Systems

Sample locations should be representative of the distribution system and include sites such as municipal buildings, public schools, airports and parks, hydrants, restaurants, theaters, gas stations, industrial plants and private residences. A systematic coverage of such points in the distribution system should detect contamination from breaks in water lines, loss of pressure, or cross connections. The sampling program should also include special sampling locations such as dead-end distribution lines that are sources of bacterial contamination, and far reaches of the distribution lines where chlorine residual may have dissipated.

The minimum number of samples which must be collected and examined each month is based upon the population density served by the distribution system. Samples should be collected at evenly spaced time intervals throughout the month. In the event of an unsatisfactory sample, repetitive samples must be collected until two consecutive samples yield satisfactory quality water. Check samples from any single point or special purpose samples must not be counted in the overall total of monthly samples required for compliance with MCL's.

The standards for microbiological quality are based upon the number of organisms allowable in a standard sample. A standard sample for the membrane filter technique is at least 100 mL. For the MPN test, a standard sample consists of five standard portions of either 10 mL or 100 mL.

14.5.5 Lakes and Impoundments

Sampling points in a recreational impoundment or lake should include inlets, sources of pollution, grids or transects across the long axis of the water body, bathing areas and outlets.

14.5.6 Stream Sampling

The objectives of the initial survey dictate the location, frequency and number of samples to be collected.

1. Selection of Sampling Sites: A typical stream sampling program includes sampling locations upstream of the area of concern, upstream and downstream of waste discharges, upstream and downstream from a tributary. Downstream sites should be located far enough below entry of discharge or tributary to allow thorough mixing. For more complex situations, where several waste discharges are involved, sampling includes sites upstream and downstream from the combined discharge area and samples taken directly from each industrial or municipal waste discharge. Using

- available bacteriological, chemical and discharge rate data, the contribution of each pollution source can be determined.
2. Small Streams: Small streams should be sampled at background stations upstream of the pollution sources and at stations downstream from pollution sources. Additional sampling sites should be located downstream to delineate the zones of pollution. Avoid sampling areas where stagnation may occur (backwater of a tributary) and areas located near the inside bank of a curve in the stream which may not be representative of the main channel.
 3. Large Streams and Rivers: Large streams are usually not well mixed laterally for long distances downstream from the pollution sources. Sampling sites below point source pollution should be established to provide desired downstream travel time and dispersal as determined by flow rate measurements. Particular care must be taken to establish the proper sampling points at: the upper reach control station, non-point sources of pollution, waste discharges as they enter the stream, quarter-point samples below the pollution sources to detect channeling, tributaries, and downstream from tributaries after mixing. Occasionally, depth samples are necessary to determine vertical mixing patterns.

14.5.7 Recreational Waters

1. Selection of Sampling Sites: Select sampling sites which reflect the quality of water throughout the recreational area. Boat marinas, waste drainage from dry well restrooms and other public buildings, upstream flows from impounded rivers or drainages into lakes, reservoirs or impounded streams, as well as the lake or body of water itself should be sampled. Sampling sites at bathing beaches or other recreational areas should include upstream or peripheral areas and locations adjacent to natural drains that would discharge storm water, or run off areas draining septic wastes from restaurants, marinas, or garbage collection areas. Swimming pool water should be monitored at least daily during maximum use periods, preferably at the overflow.
2. Depths: Sampling in bathing areas should be standardized at 1 foot for shallow depths and at 3 feet for swimming depths.
3. Frequency and Time Collect samples daily during high use seasons. Select high use days (Fridays, weekends and holidays) and sample during peak period of the day, generally in the afternoons. Sample estuarine waters at high tide, low tide and ebb tide to obtain a measure of the cyclic changes in water quality.

14.5.8 Domestic and Industrial Waste Discharges

When it is often necessary to sample secondary and tertiary wastes from municipal waste treatment plants and various industrial waste treatment operations, sampling must be adjusted to meet the specific situation.

If plant treatment efficiency varies considerably, collect grab samples around the clock at selected intervals for a three to five day period. If it is known that the process displays little variation, fewer samples are needed. The NPDES has established treatment plant effluent limits for wastewater dischargers. These are often based on maximum and mean values. A sufficient number of samples must be collected to satisfy the permit and/or provide statistically sound data and give a fair representation of the bacteriological quality of the discharge.(10)

14.5.9 Marine and Estuarine Sampling

Sampling marine and estuarine waters requires the consideration of other factors in addition to those usually recognized in fresh water sampling. They include tidal cycles, current patterns, bottom currents and counter-currents, stratification, climatic conditions, seasonal fluctuations, dispersion of discharges and multi-depth sampling

The frequency of sampling varies with the objectives. When a sampling program is started, it may be necessary to sample every hour around the clock to establish pollutional loads and dispersion patterns. The sewage discharges may occur continuously or intermittently.

When the sampling strategy for a survey is planned, data may be available from previous hydrological studies done by Coast Guard, Corps of Engineers, National Oceanic and Atmospheric Administration (NOAA), U.S. Geological Survey, or university and private research investigations. In a survey, float studies and dye studies are often used to determine surface and undercurrents. Initially depth samples are taken on the bottom and at five feet increments between surface and bottom. A random grid pattern for selecting sampling sites is established statistically.

1. Marine Sampling: In ocean studies, the environmental conditions are most diverse along the coast where shore, atmosphere and the surf are strong influences. The shallow coastal waters are particularly susceptible to daily fluctuations in temperature and seasonal changes. Sampling during the entire tidal cycle or during a half cycle may be required. Many ocean studies such as sampling over the continental shelf involve huge areas where no two areas are the same. Selection of sampling sites and depths are most critical in marine waters. In winter, cooling of coastal waters can result in water layers which approach 0°C. In summer, the shallow waters warm much faster than the deeper waters. Despite the higher temperature, oxygen concentrations are higher in shallow than in deeper waters due to greater water movement, surf action and photosynthetic activity from macrophytes and the plankton. Moving from the shallow waters to the intermediate depths, one observes a moderation of these shallow water characteristics. In the deeper waters, there is a marked stabilization of conditions.

Water temperatures are lower and more stable. Deep waters have limited turbulence little penetration of light, sparse vegetation, and layer of silt and sediment covering the ocean floor.

2. Estuarine Sampling: When a survey is made on an estuary, samples are often taken from a boat, usually making an end to end traverse of the estuary. Another method involves taking samples throughout a tidal cycle, every hour or two hours from a bridge, or from a boat anchored at a number of fixed points.

In a large bay or estuary where many square miles of area are involved, a grid or series of stations may be necessary. Two sets of samples are usually taken from an area on a given day, one at ebb or flood slack water, and the other three hours earlier, or later, at the half tide interval. Sampling is scheduled so that the mid-sampling time of each run coincides with the calculated occurrence of the tidal condition.

In locating sampling sites, one must consider points at which tributary waters enter the main stream or estuary, location of shellfish beds, and bathing beaches. The sampling stations can be adjusted as data accumulate. For example, if a series of stations one-half mile apart consistently show similar values, some stations may be dropped and others added in areas where data shows more variability.

Considerable stratification can occur in estuaries because of the differing densities of salt water and fresh water. It is essential when starting a survey of an unknown estuary to find out whether there is any marked stratification. This can be done by chloride determinations at different locations and depths. It is possible for stratification to occur in one part of an estuary and not in another.

On a flood tide, the more dense salt water pushes up into the less dense fresh river water causing an overlapping, with the fresh water flowing on top and forming the phenomenon called a salt water wedge. As a result, stratification occurs. If the discharge of pollution is in the salt water layer, the contamination will be concentrated near the bottom at the flood tide. The flow or velocity of the fresh water will influence the degree of stratification which occurs. If one is sampling only at the surface, it is possible that the data will not show the polluted underflowing water which was contaminated at a point below the fresh water river. Therefore, where stratification is suspected, samples at different depths will be needed to measure vertical distribution.

3. Shellfish-Harvesting Waters: Water overlying shellfish-harvesting areas should be sampled during periods of most unfavorable hydrographic conditions, usually at low tide after heavy precipitation. However, shellfish beds are sometimes exposed during low tide and must be sampled during other tidal conditions. Procedures for sampling of shellfish and water in shellfish growing areas are governed by the National Shellfish Sanitation Program's Manual of Operations. (11)

14.6 PRESERVATION AND TRANSIT OF SAMPLES (4)(5)

The adherence to sample preservation and holding time limits is critical to the production of valid data. Samples exceeding the limits should not be analyzed. Observe the following rules:

14.6.1 Storage Temperature and Handling Conditions

Bacteriological samples should be iced or refrigerated at a temperature of 1 to 4°C during transit to the laboratory. Insulated containers are preferable to assure proper maintenance of storage temperature. Care should be taken that sample bottle tops are not immersed in water during transit or storage.

14.6.2 Holding Time Limitations

Although samples should be examined as soon as possible after collection, they should not be held longer than six hours between collection and initiation of analyses.(12) This limit is applied to fresh waters, seawaters and shellfish-bed waters. The exception is water supply samples mailed in from water treatment systems. Current drinking water regulations permit these samples to be held up to 30 hours.

Although a holding time of six hours is permitted sewage samples, organically rich wastes and marine waters are particularly susceptible to rapid increases or die-away and should be held for the shortest time possible, to minimize change.

If the specified holding time limits cannot be observed, the following alternatives should be considered:

1. Temporary Field Laboratories: In situations where it is impossible to meet the 6 hour maximum holding time between collection and processing of samples, consider the use of temporary field laboratories located near the collection site.
2. Delayed Incubation Procedure: If sampling and transit conditions require more than 6 hours, and the use of field laboratories is impossible, consider the delayed incubation procedures for total and fecal coliforms and fecal streptococci.
3. Public Transportation: Occasionally, commercial forms of transit such as airlines, buslines or couriers are used to transport samples contained in ice chests to the laboratory. These should be considered only when storage time, temperature requirements and the proper disposition of the samples can be assured.

14.7 REFERENCES

1. Federal Water Pollution Control Act Amendments of 1972. Public Law 92-500. October 18 1972. 86 Stat. 8 16. 33 United States Code (USC). Sec. 1151.
2. Marine Protection Research and Sanctuaries Act of 1972. Public Law 92-532. October 23 1972. 86 Stat. 1052.
3. Safe Drinking Water Act. Public Law 93-523. December 16 1974. 88 Stat. 1660. 42 United States Code (USC) 300f.
4. Standard Methods for the Examination of Water and Wastewater. 15th Edition. Washington D.C. 1980 1134 pp.
5. Bordner, R.H., J.A. Winter and P.V. Scarpino. editors. Microbiological Methods for Monitoring the Environment. U.S. EPA Environmental Monitoring and Support Laboratory, Cincinnati. EPA 600/8-78-017. December 1978.
6. Shipe, E.L. and A. Fields. Comparison of the molecular filter techniques with agar plate counts for the enumeration of E. Coli in various aqueous concentrations of zinc and copper sulfate. Appl. Microbiol. 2:382 1954.
7. Shipe, E.L. and A. Fields. Chelation as a method for maintaining the coliform index in water supplies. Public Health Reports. 71:974 1956.
8. 40 CFR 141. National Interim Primary Drinking Water Regulations. December 24, 1975. pp. 59566-59585.
9. U.S. Environmental Protection Agency. Manual for the Interim Certification of Laboratories Involved in Analyzing Public Drinking Water Supplies, Criteria and Procedures. Environmental Monitoring and Support Laboratory, Cincinnati. EPA 600/8-78-008. May, 1978.
10. 40 CFR 136. Guidelines Establishing Test Procedures for Analysis of Pollutants. October 16, 1973. pp. 28758-28760. December 1, 1976. pp. 52780-52786, and further amendments.
11. Hauser, L.S. editor, 1965. National Shellfish Sanitation Program. Manual of Operations. Part 1: Sanitation of shellfish growing areas. U.S. Public Health Service Washington D.C.
12. Public Health Laboratory Service Water Subcommittee. 1953. The effect of storage on the coliform and Bacterium coli counts of water samples. Storage for six hours at room and refrigerator temperatures. J. Hyg. 51:559.

CHAPTER 15

SAMPLE CONTROL PROCEDURES AND CHAIN OF CUSTODY

The successful implementation of a monitoring program depends on the capability to produce valid data and to demonstrate such validity.(1) In addition to proper sample collection, preservation, storage and handling appropriate sample identification procedures and chain of custody are necessary to help insure the validity of the data. The procedures specified herein are those used by the Office of Enforcement, U.S. Environmental Protection Agency as of October, 1980. However, changes may occur and the reader is advised to keep abreast of official uniform procedures.(2)

A sample is physical evidence collected from a facility or from the environment. An essential part of all enforcement investigations is that evidence gathered be controlled. To accomplish this, the following sample identification and chain-of-custody procedures are recommended.

15.1 SAMPLE IDENTIFICATION

The method of identification of a sample depends on the type of measurement or analyses performed. When in-situ measurements are made, the data are recorded directly in logbooks or Field Data Records, Figure 15.1, with identifying information (project code, station numbers, station location, date, time, samplers), field observations, and remarks. Examples of in-situ measurements are pH, temperature, conductivity, and flow measurement.

Samples other than in-situ measurements, are identified by a sample tag, Figure 15.2, or other appropriate identification (hereinafter referred to as a sample tag).

These samples are transported from the sample location to a laboratory or other location for analysis. Before removal, however, a sample is often separated into portions, depending upon the analyses to be performed. Each portion is preserved in accordance with applicable procedures and the sample container is identified by a sample tag. Sample tags shall be completed for each sample, using waterproof ink, unless prohibited by weather conditions. For example, a logbook notation would explain that a pencil was used to fill out the sample tag because a ballpoint pen would not function in freezing weather. The information recorded on the sample tag includes:

Project Code - A number assigned by S & A

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF ENFORCEMENT
NATIONAL ENFORCEMENT INVESTIGATIONS CENTER
BUILDING 53, BOX 25227, DENVER FEDERAL CENTER
DENVER, COLORADO 80225



Project Code		Station No.		Mo./Day/Yr.		Time		Designate:									
								Comp.	Grab								
Station Location				Samplers: (Signature)													
Tag #	Lab Sample #	Remarks:	BOD	Antions	Solids (TSS) (TDS) (SS)	COD, TOC, Nutrients	Phenolics	Mercury	Metals	Cyanide	Oil and Grease	Organics GC/MS	Priority Pollutants	Volatile Organics	Pesticides	Mutagenicity	Bacteriology

Figure 15.2 Sample Tag (Water)

- Station Number - A number assigned by the Project Coordinator and listed in the project plan or the NPDES permit number if used for NPDES inspections.
- Date - A six-digit number indicating the year, month and day of collection.
- Time - A four-digit number indicating the military time of collection - for example 0954.
- Station Location - The sampling station description as specified in the project plan.
- Samplers - Each sampler is identified.
- Tag Number - A unique serial number is stamped on each tag that identifies Region with consecutive number - for example 8-1239.
- Remarks - The samplers record pertinent observations.

The tag used for water samples (also soil, sediment and biotic samples) contains an appropriate place for designating the sample as a grab or a composite, and identifying the type of sample collected for analyses and preservative, if any. The Project Coordinator will detail procedures for completing tags used for soil, water, sediment, and biotic samples. The sample tags are attached to or folded around each sample.

After collection, separation, identification, and preservation, the sample is maintained under chain-of-custody procedures discussed below. If the composite or grab sample is to be split, it is aliquoted into similar sample containers. Identical sample tags are completed and attached to each split and marked "Split." The tag identifies the split sample for the appropriate government agency, facility, laboratory, or company. In a similar fashion, all tags on blank or duplicate samples will be marked "Blank" or "Duplicate" respectively.

15.2 CHAIN-OF-CUSTODY PROCEDURES

Due to the evidentiary nature of samples collected during enforcement investigations, possession must be traceable from the time the samples are collected until they are introduced as evidence in legal proceedings. To maintain and document sample possession, chain-of-custody procedures are followed.

15.2.1 Sample Custody

A sample is under custody if:

1. It is in your possession, or
2. It is in your view, after being in your possession, or

3. It was in your possession and then you locked it up to prevent tampering, or
4. It is in a designated secure area

15.2.2 Field Custody Procedures

1. In collecting samples for evidence, collect only that number which provides a good representation of the media being sampled. To the extent possible, the quantity and types of samples and sample locations are determined prior to the actual field work. As few people as possible should handle samples.
2. The field sampler is personally responsible for the care and custody of the samples collected until they are transferred or dispatched properly.
3. The Project Coordinator determines whether proper custody procedures were followed during the field work and decides if additional samples are required.

15.2.3 Transfer of Custody and Shipment

1. Samples are accompanied by a Chain-of-Custody Record, Figure 15.3. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents sample custody transfer from the sampler, often through another person, to the analyst in a mobile laboratory, or at the laboratory.
2. Samples will be packaged properly for shipment and dispatched to the appropriate laboratory for analysis, with a separate custody record accompanying each shipment (for example, one for each field laboratory, one for samples driven to the laboratory). Shipping containers will be padlocked or sealed for shipment to the laboratory. The method of shipment, courier name(s) and other pertinent information are entered in the "Remarks" box.
3. Whenever samples are split with a source or government agency, it is noted in the "Remarks" section. The note indicates with whom the samples are being split and is signed by both the sampler and recipient. If either party refuses a split sample, this will be noted and signed by both parties. The person relinquishing the samples to the facility or agency should request the signature of a representative of the appropriate party, acknowledging receipt of the samples. If a representative is unavailable or refuses to sign, this is noted in the "Remarks" space. When appropriate, as in the case where the representative is unavailable, the custody record should contain a statement that the samples were delivered to the designated location at the designated time.
4. All shipments will be accompanied by the Chain-of-Custody Record identifying its contents. The original record will accompany the shipment, and a copy will be retained by the Project Coordinator.
5. If sent by mail, the package will be registered with return receipt requested. If sent by common carrier, a Government Bill of Lading will be used. Air freight shipments are sent collect. Freight bills, Post Office receipts, and Bills of Lading will be retained

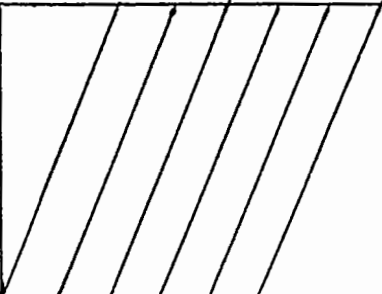
Proj. No.		Project Name				No. of con- tainers							Remarks	
Samplers: (Signature)														
Sta. No.	Date	Time	Comp.	Grab	Station Location									
Relinquished by: (Signature)			Date/Time		Received by: (Signature)		Relinquished by: (Signature)		Date/Time		Received by: (Signature)			
Relinquished by: (Signature)			Date/Time		Received by: (Signature)		Relinquished by: (Signature)		Date/Time		Received by: (Signature)			
Relinquished by: (Signature)			Date/Time		Received for Laboratory by: (Signature)			Date/Time		Remarks				

Figure 15.3 Chain of Custody Record

Figure 15.4 NPDES Compliance Inspection Report

Sections F thru L: Complete on all inspections, as appropriate. N/A = Not Applicable		PERMIT NO.
SECTION F - Facility and Permit Background		
ADDRESS OF PERMITTEE IF DIFFERENT FROM FACILITY (Including City, County and ZIP code)	DATE OF LAST PREVIOUS INVESTIGATION BY EPA/STATE	
	FINDINGS	
SECTION G - Records and Reports		
RECORDS AND REPORTS MAINTAINED AS REQUIRED BY PERMIT. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A (Further explanation attached _____)		
DETAILS:		
(a) ADEQUATE RECORDS MAINTAINED OF:		
(i) SAMPLING DATE, TIME, EXACT LOCATION	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(ii) ANALYSES DATES, TIMES	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(iii) INDIVIDUAL PERFORMING ANALYSIS	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(iv) ANALYTICAL METHODS/TECHNIQUES USED	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(v) ANALYTICAL RESULTS (e.g., consistent with self-monitoring report data)	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(b) MONITORING RECORDS (e.g., flow, pH, D.O., etc.) MAINTAINED FOR A MINIMUM OF THREE YEARS INCLUDING ALL ORIGINAL STRIP CHART RECORDINGS (e.g. continuous monitoring instrumentation, calibration and maintenance records).		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(c) LAB EQUIPMENT CALIBRATION AND MAINTENANCE RECORDS KEPT.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(d) FACILITY OPERATING RECORDS KEPT INCLUDING OPERATING LOGS FOR EACH TREATMENT UNIT.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(e) QUALITY ASSURANCE RECORDS KEPT.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(f) RECORDS MAINTAINED OF MAJOR CONTRIBUTING INDUSTRIES (and their compliance status) USING PUBLICLY OWNED TREATMENT WORKS.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
SECTION H - Permit Verification		
INSPECTION OBSERVATIONS VERIFY THE PERMIT. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A (Further explanation attached _____)		
DETAILS:		
(a) CORRECT NAME AND MAILING ADDRESS OF PERMITTEE.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(b) FACILITY IS AS DESCRIBED IN PERMIT.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(c) PRINCIPAL PRODUCT(S) AND PRODUCTION RATES CONFORM WITH THOSE SET FORTH IN PERMIT APPLICATION.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(d) TREATMENT PROCESSES ARE AS DESCRIBED IN PERMIT APPLICATION.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(e) NOTIFICATION GIVEN TO EPA/STATE OF NEW, DIFFERENT OR INCREASED DISCHARGES.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(f) ACCURATE RECORDS OF RAW WATER VOLUME MAINTAINED.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(g) NUMBER AND LOCATION OF DISCHARGE POINTS ARE AS DESCRIBED IN PERMIT.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(h) CORRECT NAME AND LOCATION OF RECEIVING WATERS.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(i) ALL DISCHARGES ARE PERMITTED.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
SECTION I - Operation and Maintenance		
TREATMENT FACILITY PROPERLY OPERATED AND MAINTAINED. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A (Further explanation attached _____)		
DETAILS:		
(a) STANDBY POWER OR OTHER EQUIVALENT PROVISIONS PROVIDED.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(b) ADEQUATE ALARM SYSTEM FOR POWER OR EQUIPMENT FAILURES AVAILABLE.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(c) REPORTS ON ALTERNATE SOURCE OF POWER SENT TO EPA/STATE AS REQUIRED BY PERMIT.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(d) SLUDGES AND SOLIDS ADEQUATELY DISPOSED.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(e) ALL TREATMENT UNITS IN SERVICE.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(f) CONSULTING ENGINEER RETAINED OR AVAILABLE FOR CONSULTATION ON OPERATION AND MAINTENANCE PROBLEMS.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(g) QUALIFIED OPERATING STAFF PROVIDED.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(h) ESTABLISHED PROCEDURES AVAILABLE FOR TRAINING NEW OPERATORS.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(i) FILES MAINTAINED ON SPARE PARTS INVENTORY, MAJOR EQUIPMENT SPECIFICATIONS, AND PARTS AND EQUIPMENT SUPPLIERS.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(j) INSTRUCTIONS FILES KEPT FOR OPERATION AND MAINTENANCE OF EACH ITEM OF MAJOR EQUIPMENT.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(k) OPERATION AND MAINTENANCE MANUAL MAINTAINED.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(l) SPCC PLAN AVAILABLE.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(m) REGULATORY AGENCY NOTIFIED OF BY PASSING. (Dates _____)		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(n) ANY BY-PASSING SINCE LAST INSPECTION.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A
(o) ANY HYDRAULIC AND/OR ORGANIC OVERLOADS EXPERIENCED.		
	<input type="checkbox"/> YES	<input type="checkbox"/> NO <input type="checkbox"/> N/A

Figure 15.4 (Continued)

	PERMIT NO.
SECTION J - Compliance Schedules	
PERMITTEE IS MEETING COMPLIANCE SCHEDULE. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A <i>(Further explanation attached _____)</i> CHECK APPROPRIATE PHASE(S): <input type="checkbox"/> (a) THE PERMITTEE HAS OBTAINED THE NECESSARY APPROVALS FROM THE APPROPRIATE AUTHORITIES TO BEGIN CONSTRUCTION. <input type="checkbox"/> (b) PROPER ARRANGEMENT HAS BEEN MADE FOR FINANCING <i>(mortgage commitments, grants, etc.)</i> . <input type="checkbox"/> (c) CONTRACTS FOR ENGINEERING SERVICES HAVE BEEN EXECUTED. <input type="checkbox"/> (d) DESIGN PLANS AND SPECIFICATIONS HAVE BEEN COMPLETED. <input type="checkbox"/> (e) CONSTRUCTION HAS COMMENCED. <input type="checkbox"/> (f) CONSTRUCTION AND/OR EQUIPMENT ACQUISITION IS ON SCHEDULE. <input type="checkbox"/> (g) CONSTRUCTION HAS BEEN COMPLETED. <input type="checkbox"/> (h) START-UP HAS COMMENCED. <input type="checkbox"/> (i) THE PERMITTEE HAS REQUESTED AN EXTENSION OF TIME.	
SECTION K - Self-Monitoring Program	
Part 1 - Flow measurement <i>(Further explanation attached _____)</i>	
PERMITTEE FLOW MEASUREMENT MEETS THE REQUIREMENTS AND INTENT OF THE PERMIT. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A DETAILS:	
(a) PRIMARY MEASURING DEVICE PROPERLY INSTALLED. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A TYPE OF DEVICE: <input type="checkbox"/> WEIR <input type="checkbox"/> PARSHALL FLUME <input type="checkbox"/> MAGMETER <input type="checkbox"/> VENTURI METER <input type="checkbox"/> OTHER <i>(Specify _____)</i>	
(b) CALIBRATION FREQUENCY ADEQUATE. <i>(Date of last calibration _____)</i> <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(c) PRIMARY FLOW MEASURING DEVICE PROPERLY OPERATED AND MAINTAINED. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(d) SECONDARY INSTRUMENTS <i>(totalizers, recorders, etc.)</i> PROPERLY OPERATED AND MAINTAINED. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(e) FLOW MEASUREMENT EQUIPMENT ADEQUATE TO HANDLE EXPECTED RANGES OF FLOW RATES. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
Part 2 - Sampling <i>(Further explanation attached _____)</i>	
PERMITTEE SAMPLING MEETS THE REQUIREMENTS AND INTENT OF THE PERMIT. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A DETAILS:	
(a) LOCATIONS ADEQUATE FOR REPRESENTATIVE SAMPLES. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(b) PARAMETERS AND SAMPLING FREQUENCY AGREE WITH PERMIT. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(c) PERMITTEE IS USING METHOD OF SAMPLE COLLECTION REQUIRED BY PERMIT. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
IF NO, <input type="checkbox"/> GRAB <input type="checkbox"/> MANUAL COMPOSITE <input type="checkbox"/> AUTOMATIC COMPOSITE FREQUENCY _____	
(d) SAMPLE COLLECTION PROCEDURES ARE ADEQUATE. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(i) SAMPLES REFRIGERATED DURING COMPOSITING <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(ii) PROPER PRESERVATION TECHNIQUES USED <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(iii) FLOW PROPORTIONED SAMPLES OBTAINED WHERE REQUIRED BY PERMIT <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(iv) SAMPLE HOLDING TIMES PRIOR TO ANALYSES IN CONFORMANCE WITH 40 CFR 136.3 <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(e) MONITORING AND ANALYSES BEING PERFORMED MORE FREQUENTLY THAN REQUIRED BY PERMIT. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(f) IF (e) IS YES, RESULTS ARE REPORTED IN PERMITTEE'S SELF-MONITORING REPORT. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
Part 3 - Laboratory <i>(Further explanation attached _____)</i>	
PERMITTEE LABORATORY PROCEDURES MEET THE REQUIREMENTS AND INTENT OF THE PERMIT. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A DETAILS:	
(a) EPA APPROVED ANALYTICAL TESTING PROCEDURES USED. <i>(40 CFR 136.3)</i> <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(b) IF ALTERNATE ANALYTICAL PROCEDURES ARE USED, PROPER APPROVAL HAS BEEN OBTAINED. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(c) PARAMETERS OTHER THAN THOSE REQUIRED BY THE PERMIT ARE ANALYZED. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(d) SATISFACTORY CALIBRATION AND MAINTENANCE OF INSTRUMENTS AND EQUIPMENT. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(e) QUALITY CONTROL PROCEDURES USED. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(f) DUPLICATE SAMPLES ARE ANALYZED. _____ % OF TIME. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(g) SPIKED SAMPLES ARE USED. _____ % OF TIME. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(h) COMMERCIAL LABORATORY USED. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
(i) COMMERCIAL LABORATORY STATE CERTIFIED. <input type="checkbox"/> YES <input type="checkbox"/> NO <input type="checkbox"/> N/A	
LAB NAME _____	
LAB ADDRESS _____	

Figure 15.4 (Continued)

						PERMIT NO.	
SECTION L - Effluent/Receiving Water Observations <i>(Further explanation attached _____)</i>							
OUTFALL NO.	OIL SHEEN	GREASE	TURBIDITY	VISIBLE FOAM	VISIBLE FLOAT SOL	COLOR	OTHER
(Sections M and N: Complete as appropriate for sampling inspections)							
SECTION M - Sampling Inspection Procedures and Observations <i>(Further explanation attached _____)</i>							
<input type="checkbox"/> GRAB SAMPLES OBTAINED <input type="checkbox"/> COMPOSITE OBTAINED <input type="checkbox"/> FLOW PROPORTIONED SAMPLE <input type="checkbox"/> AUTOMATIC SAMPLER USED <input type="checkbox"/> SAMPLE SPLIT WITH PERMITTEE <input type="checkbox"/> CHAIN OF CUSTODY EMPLOYED <input type="checkbox"/> SAMPLE OBTAINED FROM FACILITY SAMPLING DEVICE							
COMPOSITING FREQUENCY _____				PRESERVATION _____			
SAMPLE REFRIGERATED DURING COMPOSITING: <input type="checkbox"/> YES <input type="checkbox"/> NO							
SAMPLE REPRESENTATIVE OF VOLUME AND NATURE OF DISCHARGE _____							
SECTION N - Analytical Results <i>(Attach report if necessary)</i>							

Figure 15.4 (Continued)

as part of the permanent documentation.

15.3 FIELD FORMS

Appropriate field sheets must be completed at the time of sample collection. These would include NPDES Compliance Inspection Report forms (EPA Form 3560-3), Figure 15.4, (3) and Sample Tags, Figure 15.2.

In addition to sample tags and field sheets, a bound field notebook must be maintained by the survey leader to provide a daily record of significant events. All entries must be signed and dated. All members of the survey party must use this notebook. Keep the notebook as a permanent record. In a legal proceeding, notes, if referred to, are subject to cross-examination and admissible as evidence.

15.4 REFERENCES

1. Crim R.L., editor. Model State Water Monitoring Program. EPA 440/9/74/-002, U.S. Environmental Protection Agency, Washington D.C. 1974.
2. NEIC Policies and Procedures Manual, U.S. Environmental Protection Agency Office of Enforcement, National Enforcement Investigations Center, Denver, Colorado, EPA 330/9/78/001-R.
3. U.S. Environmental Protection Agency. NPDES Compliance Evaluation Inspection (MCD-75) Manual, Enforcement Division Office of Water Enforcement, Compliance Branch, Enforcement Division (EN-338), Washington, D.C. EPA January, 1981.

CHAPTER 16

QUALITY ASSURANCE

Quality assurance is an integral part of all sampling programs. The objectives of quality assurance are to assure that the data generated is:

1. Meaningful
2. Representative
3. Complete
4. Precise
5. Accurate
6. Comparable
7. Admissable as legal evidence

Data must be well documented and representative of the condition being monitored. To enable comparison with different data and with stated program objectives, data must be presented in standard units. Quality assurance for a sampling program should address all elements from sample collection to data reporting while permitting operational flexibility. A quality assurance plan should include, as an essential part, a continuing education and training program for the personnel involved in the monitoring program. This will enhance quality assurance capabilities and aid in keeping pace with the scientific advancement occurring in the field.

16.1 OBJECTIVES OF QUALITY ASSURANCE PROGRAM

For the implementation of an effective and meaningful quality assurance program it is imperative that its objectives are well defined, documented and cover all activities that affect the quality of the data. Such written objectives are needed to assure:

1. Effective participation in the quality assurance program by various personnel in different organizations involved in a sampling program.
2. Uniform direction and approach among the personnel participating in a sampling program.
3. Integrated and planned course of action.
4. Performance evaluation against stated objectives.

To meet the above objectives, one individual within the organization should be designated the Quality Assurance (QA) Coordinator. The QA Coordinator should undertake activities such as quality planning, auditing, and programs to insure reliability. The QA Coordinator should also have the responsibility for coordinating all quality assurance activity so that complete integration of the quality assurance plan is achieved.

16.2 ELEMENTS OF A QUALITY ASSURANCE PLAN (1)

The quality assurance plan will contain the following elements:

1. A policy to establish parameter analytical criteria (accuracy, precision, detection limit) for monitoring activities. Field, sample handling, and test procedures are best established only after establishment of criteria.
2. A systematic policy for selection and use of measurement and sampling methodology. Where available, approved methodology must be used. Where alternate methodology is necessary or where approved methodology does not exist, the quality assurance plan should state how the alternate or new methodology will be documented, justified, and approved for agency use.
3. Documentation of operating procedures. The QA Coordinator should establish the format for the procedures and see that the documentation is done.
4. Intra-office quality assurance audits or acceptance criteria. The QA Coordinator as part of the documented methodology of operating procedures will approve or specify the intra-office audits. Detailed quality assurance procedures are necessary for:

Personnel selection.

Sample site selection.

Sample collection, handling and preservation.

Calibration and maintenance of instruments and equipment (field and laboratory).

Intra-office audits (field and laboratory) for the data acceptance with documentation for agency data credibility.

Review and approval of data before they are released.

Scheduled intra-office audits (field and laboratory) through the QA Coordinator to assess the accuracy of field and laboratory methodology.

An audit by the QA Coordinator on a systematic basis to see that all the above activities are being done.

16.3 PERSONNEL TRAINING (1)

Successful implementation of a quality assurance plan ultimately depends upon the competence of the monitoring personnel. All personnel involved in any function affecting data quality (sample collection, analysis, data reduction and quality assurance) should have sufficient training in their appointed jobs to contribute to the reporting of complete and high quality data. The quality assurance plan should therefore provide

for periodic assessment of training needs and should describe the manner in which training is to be accomplished. This will include both in-house and external training and education.

Several methods of training are available to promote achievement of the desired level of knowledge and skill required. The following are the training methods most commonly used in the pollution control field:

16.3.1 On the Job Training (OJT)

An effective OJT program could consist of the following:

Observe experienced professionals perform the different tasks in the measurement process.

Perform tasks under direct supervision of an experienced professional.

Perform tasks independently but with adequate quality assurance checks.

16.3.2 Short-term Course Training

A number of short term courses (normally two weeks or less) are available from EPA regional offices, states, and private schools that provide knowledge and skills to more effectively implement the NPDES monitoring program.

16.3.3 Long-term Course Training

Numerous universities, colleges, and technical schools provide long-term (quarters or semester length) academic courses in wastewater treatment, analytical chemistry, environmental engineering, and other disciplines.

16.3.4 Training Evaluation

The quality assurance plan needs to address training evaluation.

Training should be evaluated in terms of: 1) the level of knowledge and skill achieved by the operator from the training, and 2) the overall effectiveness of the training, including determination of training areas that need improvement.

A good means of measuring skill improvement is to assign the trainee a work task. Accuracy and/or completeness are commonly used indicators to assess the trainee's proficiency. The tasks should be similar to the following forms:

1. Sample Collection. Trainee would be asked to list or preferably perform all steps in a sample collection for a hypothetical or real case. This would include selection of sample site, duration and

frequency of sampling, type of samples collected (grab or composite), sampling and flow measuring equipment that would provide high quality data. In addition, the trainee would be asked to perform selected calculations. Proficiency would be judged in terms of completeness and accuracy.

2. Analysis. Trainee would be provided unknown samples for analysis normally measured in the field. As defined here, an unknown is a sample whose concentrations are known to the work supervisor (OJT) or the training instructor (short-term course training) but unknown to the trainee. Proficiency would be judged in terms of accuracy.

16.4 QUALITY ASSURANCE IN SAMPLING

As a first step for quality assurance in sample collection, the sampling program should delineate the details on sampling locations, sample type, sample frequency, number of samples, duration of sampling, sample volume, sample collection methods and holding times, equipment to be used for the sample collection, sample containers, pretreatment of containers, type and amount of preservative to be used, blanks, duplicates/triplicates, spiked samples, replicates, chain of custody procedures, and any other pertinent matter which will have a bearing on the quality assurance in sample collection and handling. Guidelines on the above can be found in this manual.

Despite a well defined sampling program, appropriate sampling and field testing procedures, errors crop up due to equipment malfunction which adversely affects the quality. Therefore, as a second step for quality assurance, procedures should be developed for routine testing, maintenance and calibration of the equipment. Manufacturer's instructions are appropriate guides on these procedures. These procedures should establish routine maintenance, testing and calibration intervals, set up written procedures for maintenance, testing and calibration, list the required calibration standards, determine the environmental conditions during calibration, and generate a documentation record system. Equipment should be labeled to indicate the calibration data and when the calibration or maintenance was performed and when it expires. Table 16.1 contains a listing of quality assurance guidelines for selected field analysis, equipment calibration and documentation.(1)

As a third step in quality assurance, random control checks should be performed to make sure that appropriate sampling guidelines on sample collection, handling and chain of custody are followed by the field personnel; and deviations, if any, are rectified. Analytical quality control as an aid to quality assurance must be performed through duplicate, split, and spiked samples; sample preservative blanks, and known standard solutions, and accuracy may be evaluated using control charts. For more details on analytical quality control, refer to EPA's Handbook for Analytical Quality Control in Water and Wastewater Laboratories.(2)

TABLE 16.1 QUALITY ASSURANCE PROCEDURES FOR FIELD ANALYSIS AND EQUIPMENT (1)

Parameter	General	Daily	Quarterly
<u>1. Dissolved Oxygen</u>			
Membrane Electrode	Enter the make, model, serial and/or ID number for each meter in a log book.	<ol style="list-style-type: none"> 1. Calibrate meter using manufacturer's instructions or Winkler-Azide method. 2. Check membrane for air bubbles and holes. Change membrane and KCl if necessary. 3. Check leads, switch contacts etc. for corrosion and shorts if meter pointer remains off scale. 	Check instrument calibration and linearity using a series of at least three dissolved oxygen standards.
Winkler-Azide Method	Record data to nearest 0.1 mg/L.	Duplicate analysis should be run to check the precision of the analyst. Duplicate values should agree within ± 0.2 mg/L.	
<u>2. pH</u>			
Electrode Method	Enter the make, model, serial and/or ID number for each meter in a log book.	<ol style="list-style-type: none"> 1. Calibrate the system against standard buffer solution of known pH value at the start of a sampling run. 	Take all meters to the laboratory for maintenance, calibration and quality control checks.

(continued)

TABLE 16.1 (continued)

Parameter	General	Daily	Quarterly
<u>2. pH (continued)</u>		<ol style="list-style-type: none"> Periodically check the buffers during the sample run and record the data in the log sheet or book. Be on the alert for erratic meter response arising from weak batteries, cracked electrode, fouling, etc. Check response and linearity following highly acidic or alkaline samples. Allow additional time for equilibration. Check against the closest reference solution each time a violation is found. Rinse electrodes thoroughly between samples and after calibration. 	
<u>3. Conductivity</u>	Enter the make, model, serial and/or ID number for each meter in a log book.	<ol style="list-style-type: none"> Standardize with KCl standards having similar specific conductance values to those anticipated in the samples. Calculate the cell constant using two different standards 	<ol style="list-style-type: none"> Take all meters to lab for maintenance calibration and quality control checks. Check temperature compensation. Check date of last platinizing and replatinize if necessary.

(continued)

TABLE 16.1 (continued)

Parameter	General	Daily	Quarterly
<u>3. Conductivity</u> (continued)			
		Cell Constant = $\frac{\text{Standard Value}}{\text{Actual Value}}$ Specific Conductance = Reading multiplied by Cell Constant 2. Rinse cell after each sample to prevent carry- over.	4. Analyze NBS or EPA reference standard and record actual vs. observed readings in the log.
<u>4. Residual Chlorine</u>			
Amperometric Titration	Enter the make, model, ID and/or serial num- ber of each titration apparatus in a log book. Report results to nearest 0.01 mg/L.	Refer to instrument manufacturer's instruc- tions for proper opera- tion and calibration procedures.	Return instrument to lab for maintenance and addition of fresh, standardized reagents
Biweekly	(continued)		

TABLE 16.1 (continued)

Parameter	General	Daily	Quarterly
<u>5. Temperature</u>			
Manual	Enter the make, model, serial number and/or ID number and temperature range for each thermometer. All standardization shall be against an NBS or NBS calibrated thermometer. Readings should agree within 1°C. If enforcement action is anticipated, calibrate the thermometer before and after analysis. All data shall be read to the nearest 10°. Report data between 0°-9°C (32°-48°F) to one significant figure; between 10°-99°C (50°-210°F) to two significant figures.	1. Check for air spaces or bubbles in the column, cracks, etc. Compare with a known source if available.	Check at two temperatures against an NBS or equivalent thermometer. Enter data in a log book. Temperature readings shall agree within 1°C or the thermometer shall be replaced or recalibrated. Accuracy shall be determined throughout the expected working range of 0° to 50°C (32°C to 120°F). A minimum of three temperatures within the range should be used to verify accuracy. Preferable ranges are: 5°-10°, 15°-25°, 35°-45°C. * (41°-50°, 59°-77°, 95°-113°F)
Thermistors:	Enter the make, model, serial and/or ID number of the instrument in a log book. All standardization shall be against an NBS or NBS calibrated thermometer. Reading should agree within 1°C.	Check thermistor or sensing device for response and operation according to the manufacturer's instructions.	Accuracy shall be determined throughout the expected working range of 0° to 50°C (32°C to 120°F). A minimum of three temperatures within the range should be used to verify the accuracy.

* Initially and Bi-annually

(continued)

TABLE 16.1 (continued)

Parameter	General	Daily	Quarterly
<u>5. Temperature (continued)</u>			
Thermistors; Thermographs etc. (cont.)	If enforcement action is anticipated, refer to the procedure listed in Manual above.	Record actual vs. standard temperature in log book.	Preferable ranges are: 5 ⁰ -10 ⁰ , 15 ⁰ -25 ⁰ , 35 ⁰ -45 ⁰ C. (41 ⁰ -50 ⁰ , 59 ⁰ -77 ⁰ , 45 ⁰ -113 ⁰ F)*
<u>6. Flow Measurement</u>	Enter the make, model, serial and/or ID number of each flow measurement instrument in a log book.	Install the devices in accordance with the manufacturer's instructions and with the procedures given in this manual.	Affix record of calibration by NBS, manufacturer or other, to the instrument log.s
<u>7. Automatic Samplers</u>	Enter the make, model serial and/or ID number of each sampler in a log book.		Check intake velocity vs. head (minimum of three samples) and clock time setting vs. actual time interval.

* Initially and Bi-annually

s Annually

16.5 EPA MANDATORY QUALITY ASSURANCE PROGRAM

On May 30, 1979, the Administrator issued EPA policy requiring all Regional Offices, Program Offices, EPA Laboratories, and the States to participate in a centrally-managed Agency-wide Quality Assurance (QA) Program.(3) The stated goal of the Program is to ensure that all environmentally-related measurements which are funded by EPA or which generate data mandated by EPA are scientifically valid, defensible, and of known precision and accuracy. In a memorandum dated June 14, 1979, the Administrator specifically addressed the QA requirements for all EPA extramural projects, including contracts, interagency agreements, grants, and cooperative agreements, that involve environmental measurements. Contractor or Grantees will be required to extend the QA requirements of the contract to all subcontractors. A complete and detailed QA project plan must be submitted as a deliverable item. The QA project plan must be approved by the Project Officer and the Quality Assurance Officer and must be adhered to.

16.5.1 Quality Assurance Reports

Contracts of short duration may require only a final QA report. Contracts of longer duration may require periodic QA reports. The QA reports will be separately identified from other contractually required reports and should contain such information as:

1. Changes to QA program plan
2. Status of completion of QA project plan
3. Measures of data quality from the project
4. Significant quality problems, quality accomplishments, and status of corrective actions
5. Results of QA performance audits
6. Results of QA system audits
7. Assessment of data quality in terms of precision, accuracy, completeness, representativeness, and comparability
8. Quality-related training

16.5.2 Performance Audits

Quality Assurance Performance Audits. The inclusion of performance audits will depend on the availability of performance evaluation samples or devices for the measurements to be made. In the event that no performance evaluation samples or devices are available for the measurements involved, consideration should be given to the use of quality control or split samples for cross-comparisons of results from offerors with those of EPA. A list of QC Samples currently available from the Quality Assurance Branch, EMSL-Cincinnati, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268, is shown below:

WATER QUALITY/WATER POLLUTION SAMPLES

_____ Chlorophyll Spectro.	_____ Urea-based Pesticides
_____ Chlorophyll Fluoro.	_____ Carbaryl
_____ Demand	_____ Cycloate
_____ LAS	_____ Diuron
_____ Mineral	_____ EPTC
_____ Mun. Digested Sludge	_____ Lannate
_____ Nutrients	_____ Monuron
_____ Oil & Grease	_____ Pebulate
_____ Organo-P Pesticides	_____ Petro Hydrocarbons
_____ PCB's in Fish	_____ Phenols (4AAP Method)
_____ PCB's in Oils	_____ Residues
_____ PCB's in Sediments	_____ Trace Metals WP I
_____ Other _____	_____ Trace Metals WP II
_____ Other _____	_____ Volatile Organics

WATER SUPPLY SAMPLES

_____ WS Herbicides
_____ WS Nitrate/Fluoride
_____ WS Chl. Hyd. Pest. I
_____ WS Chl. Hyd. Pest. II
_____ WS Res. Free Chlorine
_____ WS Trace Metals
_____ WS Trihalomethanes
_____ WS Turbidity
_____ Other _____
_____ Other _____

PRIORITY POLLUTANTS

_____ Benzidines	_____ PCB's (specific Aroclors)
_____ Cyanide	_____ Aroclor 1016
_____ Chl. Hyd. Pest. WP I	_____ Aroclor 1221
_____ Chl. Hyd. Pest. WP II	_____ Aroclor 1232
_____ Haloethers	_____ Aroclor 1242
_____ Halogenated Purgeables I	_____ Aroclor 1248
_____ Halogenated Purgeables II	_____ Aroclor 1254
_____ Aromatic Purgeables	_____ Aroclor 1260
_____ Phthalate Esters	_____ Aroclor 1262
_____ Polynuclear Aromatics I	
_____ Polynuclear Aromatics II	

16.5.3 Quality Assurance Project plan

A QA project plan must address the following: (4)

1. Title Page, with provision for approval signatures
2. Table of Contents
3. Project Descriptions
4. Project Organization(s) and Responsibilities
5. QA Objectives for Measurement Data, in terms of precision, accuracy, completeness, representativeness, and comparability
6. Sampling Procedures
7. Sample Custody
8. Calibration Procedures, References and Frequency
9. Analytical Procedures
10. Data Reduction, Validation, and Reporting
11. Internal QC Checks and Frequency
12. QA Performance Audits, System Audits, and Frequency
13. QA Reports to Management
14. Preventive Maintenance Procedures and Schedule

15. Specific Procedures to be used to routinely assess data precision, representativeness, comparability, accuracy, and completeness of the specific measurement parameters involved. This section will be required for all QA project plans.
16. Corrective Action

16.6 REFERENCES

1. U.S. Environmental Protection Agency. NPDES Compliance Sampling Inspection (MCD-51) Manual, Enforcement Division, Office of Water Enforcement, Compliance Branch, May 4, 1977.
2. U.S. Environmental Protection Agency. Handbook for Analytical Quality Control in Water and Waste-water Laboratories. EPA-600/4-79-019, March, 1979.
3. U.S. Environmental Protection Agency. Guidelines and Specifications for Implementing Quality Assurance Requirements for EPA Contracts. QAMS-002/80, Office of Monitoring and Technical Support, Office of Research and Development May, 1980.
4. U.S. Environmental Protection Agency, Guidelines and Specifications for Implementing Quality Assurance Requirements for EPA Contracts, QAMS - 005/80, office of Monitoring and Technical Support, Office of Research and Development, May 1980.

CHAPTER 17

SAMPLE PRESERVATION

Other chapters in this handbook have provided guidance for all aspects of sampling through collection of the sample. Once collected, it must be analyzed immediately or stored in a container with a preservative to maintain the integrity of the sample. This chapter provides guidance on preservation methods, holding times, storage conditions and container materials.

Complete preservation of samples, either domestic sewage, industrial wastes, or natural waters, is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological changes that take place in a sample after the sample is removed from the parent source. To maintain the integrity of the sample, appropriate selection of containers, pretreatment of containers if necessary and the holding times form the integral part of the sample preservation program.

17.1 METHODS OF PRESERVATION

Methods of preservation are relatively limited and are intended generally to: 1) retard biological action; 2) retard hydrolysis of chemical compounds and complexes; and 3) reduce volatility of constituents.

Preservation methods are generally limited to chemical addition, pH control, refrigeration, and freezing. Combinations of these methods are often used for the preservation of the sample.

17.1.1 Chemical Addition

The most convenient preservative is a chemical which can be added to a sample bottle prior to sampling. When the sample is added, the preservative disperses immediately, stabilizing the parameter(s) of concern for long periods of time. When the preservative added interferes with other parameters being measured, additional samples for those parameters must be collected. For example, concentrated nitric acid added for the preservation of some of the metals would interfere with BOD, so an additional sample must be collected for BOD.

17.1.1.1 pH Control

pH control to preserve the sample is dependent upon chemical addition.

As an example, to keep metal ions in a dissolved state concentrated nitric acid is added to lower the pH to less than 2.

17.1.2 Freezing

Freezing has been the subject of many preservation studies.(1-16) It is felt by some that freezing would be a method for increasing the holding time and allowing collection of a single sample for all analysis. However, the residue solids components (filterable and nonfilterable) of the sample change with freezing and thawing.(8) Therefore, return to equilibrium and then high speed homogenization is necessary before any analysis can be run. This method may be acceptable for certain analysis but not as a general preservation method.

17.1.3 Refrigeration

Refrigeration or icing has also been studied with various results. (10-12, 17-21) This is a common method used in field work and has no detrimental effect on sample composition. Although it does not maintain integrity for all parameters, it does not interfere with any analytical methods.

17.1.4 Preservation Guidelines

For NPDES Samples, the permit holder must use specific preservatives if the sample cannot be analyzed immediately after collection. If preserved, the analyses must be conducted within a specified time frame. Guidance submitted for approval to the 304h committee, U.S. Environmental Protection Agency, is shown in Table 17.1. Because approval and subsequent publication in the Federal Register has not taken place as of publication of the handbook, the reader is urged to keep abreast of existing NPDES regulations and changes through Federal Register publications. In addition, some parameter holding times differ for drinking water samples, for example, microbiological and nitrate parameters.

Table 17.2 provides additional references and furnishes data on preservation methods, storage and holding times for different parameters found in various literature sources. However, for a specific application of the data, reference to the original publication should be made.

17.1.5 Alternative Preservation Methods

Alternative preservation methods with different preservatives or storage conditions can be used if its effectiveness can be demonstrated by supporting data through preservation studies. Such preservation studies must specify:

1. Type of water/wastewater used as a sample in the experiment
2. Type of containers used
3. Pretreatment of the container and the glassware used
4. Preservation methods used
5. Specific temperatures or temperature range used

TABLE 17.1 REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Parameter	Container ¹	Preservative ^{2, 12}	Maximum Holding Time ³
<u>Bacterial Tests</u>			
1-4. Coliform, fecal and total	P,G	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁶	6 hours
5. Fecal streptococci	P,G	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁶	6 hours
<u>Inorganic Tests</u>			
1. Acidity	P,G	Cool, 4°C	14 days
2. Alkalinity	P,G	Cool, 4°C	14 days
4. Ammonia	P,G	Cool, 4°C H ₂ SO ₄ to pH < 2	28 days
9. Biochemical oxygen demand	P,G	Cool, 4°C	48 hours
10. Biochemical oxygen demand, carbonaceous	P,G	Cool, 4°C	48 hours
12. Bromide	P,G	None required	28 days
15. Chemical oxygen demand	P,G	Cool, 4°C H ₂ SO ₄ to pH < 2	28 days

(continued)

TABLE 17.1 (continued)

Parameter	Container ¹	Preservative ^{2, 12}	Maximum Holding Time ³
<u>Inorganic Tests</u>			
16. Chloride	P,G	None required	28 days
17. Chlorine, total residual	P,G	None required	Analyze immediately
21. Color	P,G	Cool, 4°C	48 hours
23-24. Cyanide, total and amenable to chlorination	P,G	Cool, 4°C NaOH to pH >12 0.6g ascorbic acid ⁶	14 days ⁹
25. Fluoride	p	None required	28 days
27. Hardness	P,G	HNO ₃ to pH < 2	6 months
28. Hydrogen ion (pH)	P,G	None required	Analyze immediately
31. Kjeldahl and organic 43. Nitrogen	P,G	Cool, 4°C H ₂ SO ₄ to pH < 2	28 days
<u>Metals⁴</u>			
18. Chromium VI	P,G	Cool, 4°C	24 hours
35. Mercury	P,G	HNO ₃ to pH < 2	28 days

(continued)

TABLE 17.1 (continued)

Parameter	Container ¹	Preservative ^{2, 12}	Maximum Holding Time ³
Metals, except above	P,G	HNO ₃ to pH < 2	6 months
38. Nitrate	P,G	Cool, 4°C	48 hours
39. Nitrate-nitrite	P,G	Cool, 4°C H ₂ SO ₄ to pH < 2	28 days
40. Nitrite	P,G	Cool, 4°C	48 hours
41. Oil and grease	G	Cool, 4°C H ₂ SO ₄ to pH < 2	28 days
42. Organic carbon	P,G	Cool, 4°C HCl or H ₂ SO ₄ to pH < 2	28 days
44. Orthophosphate	P,G	Filter immediately Cool, 4°C	48 hours

(continued)

TABLE 17.1 (continued)

Parameter	Container ¹	Preservative ^{2, 12}	Maximum Holding Time ³
46. Oxygen, Dissolved Probe	G Bottle and top	None required	Analyze immediately
Winkler	G bottle and top	Fix on site and store in dark	8 hours
48. Phenols	G only	Cool, 4°C H ₂ SO ₄ to pH <2	28 days
49. Phosphorus (elemental)	G	Cool, 4°C	48 hours
50. Phosphorus, total	P,G	Cool, 4°C H ₂ SO ₄ to pH <2	28 days
53. Residue, total	P,G	Cool, 4°C	7 days
54. Residue, Filterable	P,G	Cool, 4°C	7 days
55. Residue, Non-filterable (TSS)	P,G	Cool, 4°C	7 days
56. Residue, settleable	P,G	Cool, 4°C	48 hours
57. Residue, volatile	P,G	Cool, 4°C	7 days

(continued)

TABLE 17.1 (continued)

Parameter	Container ¹	Preservative ^{2, 12}	Maximum Holding Time ³
61. Silica	p	Cool, 4°C	28 days
64. Specific conductance	P,G	Cool, 4°C	28 days
65. Sulfate	P,G	Cool, 4°C	28 days
66. Sulfide	P,G	Cool, 4°C, add zinc acetate plus sodium hydroxide to pH > 9	7 days
67. Sulfite	P,G	Cool, 4°C	Analyze immediately
68. Surfactants	P,G	Cool, 4°C	48 hours
69. Temperature	P,G	None required	Analyze immediately
73. Turbidity	P,G	Cool, 4°C	48 hours

(continued)

TABLE 17.1 (continued)

Parameter	Container ¹	Preservative ^{2, 12}	Maximum Holding Time ³
<u>Organic Tests</u> ⁵			
Purgeable halocarbons	G, Teflon-lined septum	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁶	14 days
Purgeable aromatics	G, Teflon-lined septum	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁶ HCl to pH < 2 ¹⁰	14 days
3,4. Acrolein and acrylonitrile	G, Teflon-lined septum	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁶ Adjust pH to 4-5 ¹¹	14 days
Phenols	G, Teflon-lined cap	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁶	7 days until extraction, 40 days after extraction

(continued)

TABLE 17.1 (continued)

Parameter	Container ¹	Preservative ^{2, 12}	Maximum Holding Time ³
Benzidines	G, Teflon-lined cap	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁶	7 days until extraction, 40 days after extraction
Phthalate esters	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Nitrosamines ⁷	G, Teflon-lined cap	Cool, 4°C store in dark 0.008% Na ₂ S ₂ O ₃ ⁶	7 days until extraction, 40 days after extraction
PCB's	G, Teflon-lined cap	Cool 4°C ⁸ pH 5-9	7 days until extraction, 40 days after extraction
Nitroaromatics and isophorone	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Polynuclear aromatic hydrocarbons	G, Teflon-lined cap	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁶ store in dark ³	7 days until extraction, 40 days after extraction
Haloethers	G, Teflon-lined cap	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ⁶	7 days until extraction, 40 days after extraction

(continued).

TABLE 17.1 (continued)

Parameter	Container ¹	Preservative ^{2, 12}	Maximum Holding Time ³
Chlorinated hydrocarbons	G, Teflon-cap	Cool, 4 ⁰ C	7 days until extraction, 40 days after extraction
87. TCDD	G, Teflon-cap	Cool, 4 ⁰ C 0.008% Na ₂ S ₂ O ₃ ⁶	7 days until extraction, 40 days after extraction
<u>Pesticides Tests</u>			
1-70. Pesticides	G, Teflon-lined cap	Cool, 4 ⁰ C pH 5-9 ⁸	7 days until extraction, 40 days after extraction
<u>Radiological Tests</u>			
1-5. Alpha, beta and radium	P,G	HNO ₃ to pH <2	6 months

(continued)

TABLE 17.1 NOTES

1. Polyethylene (P) or Glass (G).
2. Sample preservation should be performed immediately upon sample collection. For composite samples, each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.
3. Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer time. Some samples may not be stable for the maximum time period given in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show this is necessary to maintain sample stability.
4. Samples should be filtered immediately on-site before adding preservative for dissolved metals.
5. Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.
6. Should only be used in the presence of residual chlorine.
7. For the analysis of diphenylnitrosamine, add 0.008% $\text{Na}_2\text{S}_2\text{O}_3^6$ and adjust pH to 7-10 with NaOH within 24 hours of sampling.
8. The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$.
9. Maximum holding time is 24 hours when sulfide is present.
10. Sample receiving no pH adjustment must be analyzed within seven days of sampling.
11. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.
12. When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table 17.1, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

17.2 INFORMATION ON PRESERVATION AND STORAGE OF PARAMETERS IN
VARIOUS WATERS AND WASTEWATERS

Parameters	Sample type	Preservation Method	Container Material	Temperature	Holding Time
<u>DEMAND</u> <u>PARAMETERS</u>					
Biochemical Oxygen Demand (BOD)	Raw sewage	N.S.	Glass	37°C 10°C-24°C 1°C	6-12 hours (21) 12-24 hours (21) 6 days (21)
	Raw Sewage	N.S.	N.S.	4°C	Up to 1 day in composite sam- pling systems (10)
	Raw semi-treated or fully treated domestic sewage	Frozen in a mixture of acetone and dry ice or finely ground dry ice	Polyethylene	Approximately -5°C	6 months; on thawing either with warm water or at room temp- erature, analyze using seeded technique (5)
	Raw wastewater	Freezing	Polyethylene coated milk cartons	-15°C	236 days, analyze using seeded technique (8)
	1:4 settled sewage to water from a natural stream	60-80 mg/L HgCl ₂	Plastic	Room temper- ature	18 days (22)
	Raw sewage	890 mg/L HgCl ₂	Plastic	Room temper- ature	43 days (23)

N.S.-Not Stated.

(continued)

TABLE 17.2 (continued)

Parameters	Sample type	Preservation Method	Container Material	Temperature	Holding Time
<u>DEMAND PARAMETERS</u>					
Chemical Oxygen Demand (COD)	1:4 settled sewage to water from a natural stream	60-80 mg/L HgCl_2	Plastic	Room temperature	18 days (22)
	Raw sewage	890 mg/L HgCl_2	Plastic	Room temperature	43 days
	Raw sewage	N.S.	Glass	37°C	6-12 hours (21)
				10°C-24°C	12-24 hours (21)
				1°C	6 days (21)
	Raw sewage	N.S.	N.S.	4°C	Several days (10)
Dissolved oxygen (DO)	Sea water	0.5% Chloroform + 0.5% phenol	Glass	22°C	20 days (24)
	Sea water	Acidulating water to pH 1.5 with 2.5 mL H_2SO_4 ; 5 mL HCl per liter of sample	Glass	22°C	22 days (24)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
<u>DEMAND</u>					
<u>PARAMETER</u>					
Total Organic Carbon (TOC)	Settled sewage, biological filter effluent	1 mL saturated Ag_2SO_4 solution (i.e. 4 mg of Ag^+) to a liter of sample	Glass	Refrigerate at 4°C	3 days (25)
<u>METALS:</u>					
Aluminum	Waters in the zone of mixing of river and sea waters in estuaries	Samples frozen rather than acidified	Polyethylene	-20°C	In dark, 14 days (26)
	Natural fresh water	1 mL 4M H_2SO_4 per 100 mL sample and filtered through glass-fiber filters	Polyethylene	Room temperature	4 weeks (27)
Cadmium	Stock aqueous solutions prepared in laboratory	Acidification to pH 2 with HNO_3	Polyethylene and borosilicate glass	N.S.	32 days (28)
Lead	Stock aqueous solutions prepared in laboratory	Acidification to pH 2 with HNO_3	Borosilicate glass	N.S.	24 days (28)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
<u>METALS: (cont.)</u>					
Mercury	Distilled water solutions containing 0.1-10.0	Acidified with 5% (v/v) HNO_3 + .05% Cr_2O_7	Polyethylene	N.S.	10 days (29)
	Distilled water solutions containing 0.1-10.0	Acidified with 5% (v/v) HNO_3 + .01% Cr_2O_7	Glass	N.S.	5 months (29)
Potassium	1:4 settled sewage and natural stream water	Approx. 1.5 mL saturated HgCl_2 per liter of sample (60-80 mg/L HgCl_2)	Plastic	Room Temperature	18 days (22)
Silver	Stock aqueous solutions prepared in laboratory	Acidification to pH 2 with HNO_3	Polyethylene	Room temperature	36 days (28)
Sodium	1:4 settled sewage and natural stream water	Approx. 1.5 mL saturated HgCl_2 per liter sample (60-80 mg/L HgCl_2)	Plastic	Room temperature	18 days (22)
Zinc	Stock aqueous solutions prepared in laboratory	Acidification to pH 2 with HNO_3	Polyethylene preferred over borosilicate glass	N.S.	60 days (28)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
<u>METALS:</u> (cont.)					
Cadmium	Natural lake water	Acidified to pH 1	Pyrex glass and polyethylene	-15°C	184 days (30)
Copper	Natural lake water	Acidified to pH 1	Pyrex glass and polyethylene	-15°C	184 days (30)
		.25 mL 3.5 N nitric acid after arrival at the laboratory	25 mL glass vials with polyethylene snap-caps	Room temperature	1 year (31)
Manganese	Natural lake water	Acidified to pH 1	Pyrex glass and polyethylene	-15°C	184 days (30)
Zinc	Natural lake water	Acidified to pH 1	Pyrex glass and polyethylene	-15°C	184 days (30)
		.25 mL 3.5 N nitric acid after arrival at the laboratory	25 mL glass vials with polyethylene snap-caps	Room temperature	1 year (31)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
<u>NUTRIENTS:</u>					
Ammonia Nitrogen	Relatively unpolluted bay waters	40 mg Hg ⁺² per liter of sample	Plastic	4°C	30 days (12)
	Sea waters (off shore)	0.4 g phenol per 100 mL of sample	Glass	N.S.	2 weeks (14)
		Slow freezing	Polyethylene	Frozen	20 days (14)
	Near shore and estuarine waters (filtered and fortified samples)	Freezing	Glass tubes polyseal caps	-23°C	3 months (7)
	Synthetic fresh water, unpolluted fresh water, (filtered) chemically treated domestic sewage, polluted sea water (filtered)	Unpreserved	Polyethylene	4°C	1-3 days (32)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
<u>NUTRIENTS:</u>					
Ammonia Nitrogen	Strongly polluted water	Approx. 1.5 mL saturated HgCl_2 per liter (75 mg/L)	Plastic	Room Temperature	18 days (22)
	Strongly polluted water	Approx. 3.0 mL 40% formalin solution per liter of sample (890 mg/L)	Plastic	Room Temperature	18 days (22)
	Raw Sewage	890 mg/L HgCl_2	N.S.	N.S.	43 days (23)
	Surface runoff	Freezing	Plastic	-20°C	In dark, 12 wks.
		Refrigeration	Plastic	4°C	In dark, 12 wks. (33)
		Phenylmercuric acetate (PMA): 20 mg PMA per liter of sample	Plastic	4°C	In dark, 12 wks. (33)
	Amended and unamended river water	40 mg HgCl_2 per liter of sample	Plastic	-20°C	In dark, 12 wks. (33)
		Freezing	Plastic	4°C	In dark, 12 wks. (33)
		Phenylmercuric acetate (PMA): 20 mg PMA per liter of sample	Plastic	4°C or 23°C	In dark, 12 wks. (33)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
<u>NUTRIENTS:</u> (cont.)					
Ammonia (soluble) (cont.)	Tile drainage water	Freezing	Plastic	-20°C	In dark, 12 wks. (33)
		Phenylmercuric acetate (PMA): (20 mg PMA per liter of sample)	Plastic	4°C	In dark, 12 wks. (33)
		40 mg HgCl ₂ per liter of sample	Plastic	4°C	In dark, 12 wks. (33)
Kjeldahl nitrogen	Relatively unpol- luted bay waters	40 mg Hg+2 per liters of sample	Plastic	4°C	7 days (12)
	Synthetic fresh water, unpolluted fresh water chem- ically treated do- mestic sewage and polluted sea water	Unpreserved	Polyethylene	4°C	Up to 3 days (34)
		1 mL 0.02% mercury (II) chloride per 100 mL of sample	Polyethylene	4°C	Up to 3 days (34)
	Strongly polluted water	Approx. 1.5 mL of saturated HgCl ₂ per liter (75 mg/L)	Plastic	Room Temp.	18 days (22)
	Raw manure slur- ries, oxidation ditch mixed liquor	Freezing and fast thawing or slow thawing	Whirl pack bags	N.S.	5 weeks (35)
		Refrigeration	Whirl pack bags	6-10°C	5 weeks (35)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
<u>NUTRIENTS:</u> (cont.)					
Kjeldahl nitrogen (cont.)		Acidification	Whirl pack bags	6-10°C	5 weeks (35)
		conc H ₂ SO ₄ to pH 2		6-10°C	5 weeks (35)
Nitrate Nitrogen	Relatively unpolluted fresh water (filtered), chemically treated domestic sewage, polluted sea water (filtered)	40 mg Hg ⁺²	Plastic	4°C	Up to 3 days (34)
		1 mL 0.02% mercury (II) chloride per liter of sample	Polyethylene	4°C	28 days (34)
	4 to 1 mixture of surface water and settled sewage	22 or 66 mg mercury (II) chloride per liter of sample	Glass	22±2°C	3 weeks (36)
	Strongly polluted water sample	Approx. 1.5 mL saturated mercury (II) chloride solution per liter (i.e. 60-80 mg/L of mercury (II) chloride)	Plastic	Room Temp.	18 days (22)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
<u>NUTRIENTS:</u> (cont.)					
Nitrate Nitrogen (cont.)		Approx. 3.0 mL 40% formalin solution per liter sample (890 mg/L)	Plastic	Room Temp.	18 days (22)
	Surface runoff, tile drainage water, river water	Freezing	Plastic	-20°C	In dark, 12 wks. (33)
		20 mg PMA per liter sample	Plastic	4°C or 23°C	In dark, 12 wks. (33)
	Surface runoff	40 mg HgCl ₂ per liter of sample	Plastic	4°C	In dark, 3 wks. (33)
Nitrite Nitrogen	Strongly polluted water	Approx. 1.5 mL of saturated mercuric chlo- ride solution per liter sample (i.e. 60-80 mg/L mercuric chloride)	Plastic	Room Temp.	18 days (22)
		Approx. 3.0 mL 40% formalin solution per liter sample (890 mg/L)	Plastic	Room Temp.	18 days (22)
	Sea water (fil- tered) and nitrate enriched	Freezing	Pyrex glass	-18°C	220 days (4)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
<u>NUTRIENTS:</u> (cont.)					
Nitrite Nitrogen (cont.)	Lake water (unenriched)	1 mL saturated mercuric chlo- ride per liter sample	Glass	Refrigerated at 7°C	11 days (20)
	Lake water (enriched with nitrite)	1 mL saturated mercuric chlo- ride solution per 300 mL sample	Glass	Refrigerated at 6°C	6 days (20) 6 days (20)
	Relatively un- polluted bay waters	40 mg Hg ⁺² per liter sample	Plastic	4°C	7 days (12)
	4 to 1 mixture of surface water and settled sewage	66 mg of mercury (II) chloride per liter of sample	Glass	22±2°C	45 days (36)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
<u>NUTRIENTS:</u> (cont.)					
Orthophosphate or total phosphate	Waters containing algae	Refrigeration	N.S.	3-5°C	Overnight (11)
	Polluted fresh water, polluted sea water, strongly polluted sea water, biologically treated sewage	1 mL 8N sulfuric acid per 100 mL filtered sample	Polyethylene	N.S.	For samples that cannot be analyzed within 8 hrs. (37)
	Estuarine waters	40 mg Hg ⁺² per liter sample	Glass	-10°C	One month (12)
		40 mg Hg ⁺² per liter sample	Glass	4°C	Few days (12)
	Strongly polluted waters	Approx. 1.5 mL saturated HgCl ₂ per liter (75 mg/L)	Plastic	Room Temp.	18 days (22)
Soluble Inorganic Phosphorus (SIP)	Surface runoff	N.S.	N.S.	2°C	3 days (37)
	Slow freezing and sediment removed by centrifugation	N.S.	N.S.	-20°C	3 days (37)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
<u>NUTRIENTS:</u> (cont.)					
Soluble Inorganic Phosphate	Surface runoff, tile drainage	Freezing	Plastic	-20°C	In dark, 12 wks. (33)
		Phenylmercuric acetate (PMA) 20 mg PMA per liter of sample	Plastic	4°C	In dark, 6 wks. (33)
		40 mg HgCl ₂ per liter sample	Plastic	4°C	In dark, 6 wks. (33)
	Ammended river water (45 mL river water + 5 mL of solution containing 100 ppm NH ₄ -N, 100 ppm of NO ₃ -N and 5 ppm of orthophosphate), and natural rainwater	Freezing	Plastic	-20°C	In dark, 12 wks. (33)
		40 mg HgCl ₂ per liter sample	Plastic	4°C	In dark, 12 wks. (33)
	Sea water	Addition of Chloroform (0.6-0.8% v/v) before freezing	Polyethylene	-5 to -10°C	Stored until thawed for analysis (38)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
PHYSICAL/MINERAL					
Alkalinity	1:4 settled sewage to natural stream water	Approx. 1.5 mL saturated mercuric chloride solution per liter sample (60-80 mg/L HgCl_2)	Plastic	Room temp. (Not in dark)	18 days (22)
Chloride	1:4 settled sewage and natural stream water	Approx. 1.5 mL saturated mercuric chloride solution per liter sample (60-80 mg/L HgCl_2)	Plastic	Room temp. (Not in dark)	18 days (22)
	Raw sewage	890 mg/L HgCl_2	N.S.	N.S.	43 days (23)
Conductivity	1:4 settled sewage and natural stream water	Approx. 1.5 mL saturated mercuric chloride solution per liter sample (60-80 mg/L HgCl_2)	Plastic	Room temp. (Not in dark)	18 days (22)
	Raw sewage	890 mg/L HgCl_2	N.S.	N.S.	43 days (23)
Total hardness	1:4 settled sewage and natural stream water	Approx. 1.5 mL saturated mercuric chloride solution per liter sample (60-80 mg/L HgCl_2)	Plastic	Room temp. (Not in dark)	18 days (22)

(continued)

TABLE 17.2 (continued)

Parameters	Sample Type	Preservation Method	Container Material	Temperature	Holding Time
PHYSICAL/MINERAL (cont.)					
Magnesium hardness	Raw sewage	890 mg/L HgCl_2	N.S.	N.S.	43 days (23)
Phenols	All types of water and wastewaters	1.5 mL of 1N NaOH per liter	N.S.	N.S.	(39)
	All types of water and wastewaters	N.S.	Stoppered glass bottles	N.S.	preferably to analyze shortly after collection (19)
Sulfate		3 mL 10% CuSO_4 solution per liter sample	Stoppered glass bottles	Refrigeration	Analyze within 2 days (19)
	1:4 settled sewage and natural stream water	Approx. 1.5 mL saturated mercuric chloride solution per liter (60-80 mg/L HgCl_2)	Plastic	Room Temp. (Not in dark)	18 days (22)
	Raw sewage	890 mg/L HgCl_2	N.S.	N.S.	43 days (23)

6. Duration of storage
7. Stored in light or darkness
8. Quality Control Samples - spikes, duplicates.
9. Blanks - controls
10. Number of samples analyzed, and results
11. Statistical analysis, precision and accuracy

17.2 CONTAINERS

A variety of factors affect the choice of containers and cap material. These include resistance to breakage, size, weight, interference with constituents, cost and availability. There are also various procedures for cleaning and preparing bottles depending upon the analyses to be performed on the sample.

17.2.1 Container Material

The two major types of container materials are plastic and glass.(22)

Glass:

1. Kimax Or Pyrex brand - borosilicate
2. Vycor - generally lab ware
3. Ray-Sorbor Low-Actinic - generally lab ware
4. Corex - generally lab ware

Plastic:

1. Conventional polyethylene
2. Linear polyethylene
3. Polypropylene
4. Polycarbonate
5. Rigid polyvinyl chloride
6. Teflon

All these materials have various advantages and disadvantages. Kimax or Pyrex brand borosilicate glass is inert to most materials and is recommended where glass containers are used. Conventional polyethylene is to be used when plastic is acceptable because of reasonable cost and less absorption of metal ions. The specific situation will determine the use of glass or plastic. However, use glass containers for pesticides, oil and grease, and other organics. Table 17.3 summarizes the advantages and disadvantages of these materials.

17.2.2 Container Caps

There are two major types of plastic used in container caps: polyethylene and bakelite with liners. Polyethylene caps are recommended for ease of cleaning unless oil and grease analyses are to be performed. Caps with Teflon liners should be used for pesticides and oil and grease samples. Silicone rubber material should be avoided for Trace Metals because of Zinc contaminations.(40) There are three liner types available and the advantages/disadvantages are listed in Table 17.4.

TABLE 17.3 COMPARISON OF GLASS AND
PLASTIC CONTAINERS

	Borosilicate Glass	Conventional Polyethylene
Interference with sample	Inert to all constituents except strong alkali	Good for most constituents except organics and oil and grease
Weight	Heavy	Light
Resistance to breakage	Very fragile	Durable
Cleaning	Easy to clean	Some difficulty in removing adsorbed components
Sterilizable	Yes	In some instances
Space	Takes up considerable space	Cubitainers - Substantial space savings during extended field studies.

17.2.3 Container Structure

Use a wide mouth container in most instances. This structure will permit easy filling and sample removal. It is also easily cleaned, quickly dried, and can be stored inverted. Use a narrow neck bottle when interaction with the cap liner or outside environment is to be minimized. Use a Solvent cleaned glass container for pesticide sample collection.(24)

17.2.4 Disposable Containers

Use disposable containers when the cost of cleaning is high. These containers should be precleaned and sterile. The most commonly used disposable container of this type is the molded polyethylene cubitainer shipped nested and sterile to the buyer. However since their cubic shape and flexible sides make them almost impossible to clean thoroughly, use these containers only once.

17.2.5 Container Washing

The following procedure should be followed to wash containers and caps for inorganic and general parameters:

1. Wash containers and caps with a non-phosphate detergent and scrub strongly with a brush (if possible wash liners and caps separately).
2. Rinse with tap water, then distilled water.

TABLE 17.4 COMPARISON OF CAP LINERS

Liner Type	Advantages	Disadvantages
Wax coated paper	Generally applicable to most samples, Inexpensive	Must be inspected prior to each because of deterioration. Cannot use with organics
Neoprene	Same as wax coated paper	Same as wax coated paper
Teflon	Applicable for all analyses Minimizes container/sample interaction	High cost

3. Invert to drain and dry.
4. Visually inspect for any contamination prior to storage.
5. If the container requires additional cleaning, rinse with a chromic acid solution (35 mL saturated sodium dichromate solution in 1 liter of sulfuric acid - this solution can be reused). Then rinse with tap water and distilled water and dry as indicated above.

17.2.6 Container Preparation

For certain parameters, a special cleaning procedure is needed to avoid adsorption or contamination due to interaction with container walls. These procedures are outlined below:

1. Metals: If metals are to be analyzed, rinse the container with a solution of one part nitric acid to four parts water, then with distilled water. If phosphorus is to be analyzed, rinse the container with a solution of one part hydrochloric acid to one part water, followed by distilled water. Treat the caps similarly.
2. Organics: If Oil and Grease or Pesticides are to be analyzed, rinse the sample container with methylene chloride, followed by acetone. For Pesticide analysis, use pesticide grade hexane or acetone. The container should have been previously cleaned with chromic acid solution as described in Section 17.2.5. Treat the container caps similarly.
3. Sterilization: For microbiological analyses, sterilize the container and its stopper/cap by autoclaving at 121°C for 15 minutes or by dry heat at 180°C for two hours. Heat-sensitive plastic bottles may be sterilized with ethylene oxide at low temperatures. Wrap bottles in kraft paper or cover with aluminum foil before sterilization to protect against contamination. An acceptable alternative for emergency or field use is sterilization of containers by boiling in water for 15 minutes.

17.3 HOLDING TIME

Holding time is the time interval between collection and analysis. In general, the shorter the time that elapses between collection of a sample and its analysis, the more reliable will be the analytical results.

It is impossible to state exactly how much time may be allowed to elapse between collection of a sample and its analysis; this depends on the character of the sample, particular analysis to be made, and the conditions of the storage.

For NPDES purposes, in accordance with Federal Register, part 136 follow the recommendations given in Table 17.1, and keep abreast of revised holding times that will be published in the Federal Register.

For information purposes, however, data relating to holding times for general and inorganic parameters was collected from various literature sources and is tabulated in Table 17.2.

17.4 SAMPLE VOLUME

The volume of sample collected should be sufficient to perform all the required analyses plus an additional amount to provide for any quality control needs, split samples or repeat examination. Although the volume of sample required depends on the analyses to be performed, the amount required for a fairly complete analysis is normally about eight liters, (about two gallons). The laboratory receiving the sample should be consulted for any specific volume requirements. Individual portions of a composite sample should be at least 100 milliliters in order to minimize sampler solids bias. Depending on the sampling frequency and sample volume, the total composited sample should be a minimum of 8 liters (about 2 gallons). Refer to EPA's Methods for Chemical Analysis of Water and Wastes 1979, EPA 600/4-79-020, for the sample volumes required for specific types of pollutant analyses.

17.5 REFERENCES

1. Collier, A.W. and K.T. Marvin. Stabilization of the Phosphate Ratio of Sea Water by Freezing. U.S. Government Printing Office, Washington, 71-76, 1953.
2. May, B.Z. Stabilization of the Carbohydrate Content of Sea Water Samples. Limnology and Oceanography, 5: 342-343, 1960.
3. Heron, J. Determination of Phosphate in Water after Storage in Polyethylene. Limnology and Oceanography, 5: 316-321, 1960.
4. Procter, R.R. Stabilization of the Nitrite Content of Sea Water By Freezing. Limnology and Oceanography, 7: 479-480, 1962.

5. Fogarty, W.J. and M.E. Reeder. BOD Data Retrieval Through Frozen Storage. Public Works, 88-90, March, 1964.
6. Morgan, F. and E.F. Clarke. Preserving Domestic Waste Samples by Freezing. Public Works, 73-75, November, 1964.
7. Marvin, K.T. and R.R. Proctor. Stabilizing the Ammonia-Nitrogen Content of Estuarine and Coastal Waters by Freezing. Limnology and Oceanography, 10: 288-289, 1965.
8. Zanoni, A.E. Use of Frozen Wastewater as a Test Substrate. Public Works, 72-75, November, 1965
9. Tyler, L.P. and E.C. Hargrave. Preserving Sewage Seed for BOD Analysis. Water and Sewage Works, 12: 181-184, May, 1965.
10. Agardy, F.J. and M.L. Kiado. Effects of Refrigerated Storage on the Characteristics of Wastes. Industrial Waste Conference (21st) Purdue University, 1966.
11. Fitzgerald, G.P. and S.L. Faust. Effect on Water Sample Preservation Methods on Release of Phosphorous From Algae. Limnology and Oceanography, 12: 332-334, 1967.
12. Jenkins, D. The Differentiation, Analysis and Preservation of Nitrogen and Phosphorous Forms in Natural Waters. Advances in Chemistry Series 73. American Chemical Society, Washington, D.C., 265-279, 1968.
13. Philbert, F.J. The Effect of Sample Preservation by Freezing Prior to Chemical Analysis of Great Lakes Water. Proc 16th Conference. Great Lakes Res. 282-293, 1973.
14. Degobbis, D. On the Storage of Sea Water Samples for Ammonia Determination. Limnology and Oceanography, 15: 146-150. January, 1970.
15. Burton, J.D. Problems in the Analysis of Phosphorus Compounds. Water Research, Great Britain, 7: 291-307, 1973.
16. Harms, L.L., J.N. Dornbush and J.R. Anderson. Physical and Chemical Quality of Agricultural Land Runoff. Journal WPCF, 46: 2460-2470, November, 1974.
17. Phillips, G.E. and W.D. Hatfield. Preservation of Sewage Samples. Water Works and Sewage Journal, 285-288, June, 1941.
18. Moore, E.W. Long Time Biochemical Oxygen Demands at Low Temperature. Sewage Works Journal, 13 (3): 561-577, May, 1941.
19. Ettinger, M.B., S. Schott and C.C. Ruchott. Preservation of Phenol Content in Polluted River Water Samples Previous to Analysis. Journal-AWWA, 35: 299-302, March, 1943.

20. Brezonik, P.L. and G.F. Lee. Preservation of Water Samples for Inorganic Nitrogen Analysis with Mercuric Chloride. *Air and Water Pollution (Great Britain)*, 10: 549-553, 1966.
21. Loehr, R.C. and B. Bergeron. Preservation of Wastewater Samples Prior to Analysis. *Water Research (Great Britain)* 1: 557-586, 1967.
22. Hellwig, D.H.R. Preservation of Water Samples. *International Journal of Air Water Pollution*, 8: 215-228, 1964.
23. Zobell, C.E. and B.F. Brown. Studies on the Chemical Preservation of Water Samples. *Journal of Marine Research*, 5 (3): 178-182, 1976.
24. Hellwig, D.H.R. Preservation of Waste Water Samples. *Water Research*, 1: 79-91, 1976.
25. Van Steendeven, R.A. Parameters Which Influences the Organic Carbon Determination in Water. *Water South Africa*, 2 (4): 156-159, 1976.
26. Hydes, D.J. and P.S. Liss. Fluorimetric Method for the Determination of Low Concentrations of Dissolved Aluminum in Natural Waters. *Analyst*, 101: 922-931, December, 1976.
27. Dale, T. and A. Henricksen. Intercalibration Methods for Chemical Analysis of Water. *Vatten*, (1): 91-93, 1975.
28. Struempfer, A.W. Adsorption Characteristics of Silver, Lead, Cadmium, Zinc, and Nickel on Borosilicate Glass, Polyethylene and Polypropylene Container Surfaces. *Analytical Chemistry*, 45 (13): 2251-2254, 1972.
29. Feldman, C. Preservation of Dilute Mercury Solutions. *Analytical Chemistry*. 31: 99-102, July, 1974.
30. Clement, J.L. Preservation and Storage of Water Samples for Trace Element Determination. Department of Civil Engineering, University of Illinois, Urbana, Illinois, 1972. 40 pp.
31. Henricksen, A. and Balmer. Sampling, Preservation and Storage of Water Samples for Analysis of Metals. *Vatten*: (1): 33-38, 1977.
32. Dahl, I. Intercalibration of Methods for Chemical Analysis of Water. *Vatten*. (4): 336-340, 1973.
33. Klingaman, E.D.M. and D.V. Nelson. Evaluation of Methods for Preserving the Levels of Soluble Inorganic Phosphorus and Nitrogen in Unfiltered Water Samples. *Journal Environmental Quality*, 5 (1): 42-46, 1976.
34. Dahl, I. Intercalibration of Methods for Chemical Analysis of Water. *Vatten* (2): 180-186, 1974.

35. Prakasam, T.B.S. Effects of Various Preservation Techniques on the Nitrogen Profile of Treated and Raw Poultry Waste. Draft Copy, 1975.
36. Howe, L.H. and C.W. Holley. Comparison of Mercury (II) Chloride and Sulfuric Acid as Preservatives for Nitrogen Forms in Water Samples. Environmental Science and Technology, 3 (5): 478-481, May, 1969.
37. Nelson, D.W. and M.J.M. Roomkens. Suitability of Freezing as a Method of Preserving Run Off Samples for Analysis of Soluble Phosphate. Journal Environmental Quality, 1 (3): 323-324, 1972.
38. Gilmartin, M. Changes in Inorganic Phosphate Concentration Occurring During Seawaste Sample Storage. Limnology and Oceanography, 12: 325-328, 1967.
39. Baylis, J.E. Procedure for Making Quantitative Phenol Determinations. Water Wastes and Sewage, 79: 341, 1932.
40. Gibb, R.R. Contamination by Oceanographic Samplers. Analytical Methods in Oceanography, Advances in Chemistry Series 147, American Chemical Society, 1975.

APPENDIX A - POPULATION PARAMETERS

I. Populations and Samples (1)(3)

Most sampling is done on a non-continuous basis, and so the data gathered give an incomplete picture of the true condition of a water or wastewater. If monitoring were done continuously, the data would be presented as a curve ($f(t)$, where f is the function which gives the value of the parameter at time t) rather than as a discrete set of points (numbers). Therefore, the definitions of mean and variance given in Section 4.1.1 could not be applied. This continuous function defines a "population" from which samples are taken. This population has a mean and a variance of which the sample mean and sample variance (which are the mean and variance defined in Section 4.1.1) are only estimators. This is why it is best to take as many samples as possible -- more data reveals more information about the population.

The Population Mean

The population mean, μ_x , is defined by:

$$\mu_x = E(X) = \int_{-\infty}^{\infty} x f_X(x) dx, \quad \text{where } E(X) \text{ is}$$

another expression for the mean and is read "the expected value (or expectation) of X ".

$f_X(x)$ is the density function of x , which is a function defining the distribution of X .

The Population Variance

The variance σ_x^2 , of the population is defined by:

$$\sigma_x^2 = \text{Var}(X) = E((X - \mu_x)^2) = \int_{-\infty}^{\infty} (x - \mu_x)^2 f_X(x) dx$$

As with the sample standard deviation, the population standard deviation is just the square root of the population variance

$$(\sigma_x = \sqrt{\sigma_x^2}).$$

APPENDIX B

Areas Under the Normal Curve (1)(3)

The graph of the probability density function of the standard normal distribution:

$$f_X(x) = \frac{1}{\sqrt{2\pi}} \exp(-x^2/2), \quad \text{is shown in Figure 4.6.}$$

It is the familiar bell-shaped curve. For any point z , the area under the curve to the left of z is determined by

$$\int_{-\infty}^z f_X(t) dt, \text{ which has been seen to be } P(Z \leq z), \text{ where } Z \sim N(0,1).$$

It is also known that the area to the right of z is $P(Z > z)$. The normal distribution is symmetric about its mean, and so $P(Z > \mu_Z + c) = P(Z < \mu_Z - c)$ for any constant c , which in the case of the standard normal distribution, in which the mean is zero, reduces to $P(Z > c) = P(Z < -c)$.

There is a property of probabilities which says that, under certain conditions which are not discussed here, $P(Z > c \text{ or } Z < -c) = P(Z > c) + P(Z < -c) = 2P(Z > c)$ and so if $P(Z > c \text{ or } Z < -c) = 2\alpha$ then $P(Z > c) = \alpha$, which is the area of the shaded region in Figure 4.8.

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati, OH 45268

Postage and
Fees Paid
Environmental
Protection
Agency
EPA-335



Official Business
Penalty for Private Use, \$300

Special Fourth-Class Rate
Book

Please make all necessary changes on the above label,
detach or copy, and return to the address in the upper
left-hand corner.

If you do not wish to receive these reports CHECK HERE ☐
detach, or copy this cover, and return to the address in the
upper left-hand corner.

EPA-600/4-82-029